TEXT-BOOKS OF SCIENCE

ADAPTED FOR THE USE OF

ARTISANS AND STUDENTS IN PUBLIC AND SCIENCE SCHOOLS.

CHEMICAL PHILOSOPHY.

INTRODUCTION TO THE STUDY

OF

CHEMICAL PHILOSOPHY

THE PRINCIPLES

OF

THEORETICAL AND SYSTEMATIC CHEMISTRY

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PREFACE.

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This little volume is primarily intended for the use of students. It aims at presenting a synopsis, brief indeed, and probably imperfect, of the leading principles of chemistry in such a form as to give the subject a more decided educational direction than has been hitherto customary.

In consideration of its peculiar fitness for developing the powers of observation, of reasoning, and of memory, no branch of experimental science deserves more emphatic recognition at the hands of educators than chemistry. In order, however, that its advantages may be reaped to the full, I believe that the methods of teaching very generally prevalent in schools require to be considerably modified. I think teachers ought to realise the fact that chemistry, as a school subject, is not taught with a view to its practical applications to medicine, manufactures, or the arts, but because the study is calculated to quicken the faculties of observation, to strengthen the memory, and to engender a power and a

habit of continuous thought, as well as to arouse new interests and open up new fields to the imagination. It is of little consequence, in this view, whether or not the facts acquired can be turned to practical account ; but it is of prime importance that the phenomena brought under their notice, and the manner in which those phenomena are presented, should be such as will compel the pupils to think.

Notwithstanding that the book does not profess to be a complete treatise on the subject, its contents will, I believe, be found sufficiently comprehensive to afford a tolerably general view of chemical theory as it exists at the present time. My desire has been to assist the student in attaining to broad and philosophic views of chemistry as a whole, and to accustom him to regard it as one out of many branches of physical science rather than as a mystery standing apart from other studies.

My little text-book embodies the substance of the lectures I have been giving for some time past to the more advanced classes in Clifton College. Notwithstanding that some portions of the book deal with subjects which are outside the course of ordinary elementary teaching, and must be admitted to be rather more difficult, I have not found them beyond the capacity of intelligent boys of fifteen to eighteen years of age, and I have every reason to be satisfied with the results hitherto obtained.

The use which I propose to make of the book in my own teaching is to get the more advanced classes to read it by small portions at a time, and to work out all the exercises, which, it must be understood, are merely sugges- tive, and will require to be copiously supplemented by any teacher who adopts the work. Such a course of study obviously cannot be undertaken except as the sequel to a series of experimental lessons, perhaps repeated more than once, in which the properties of the chief elements and some of their compounds have been demonstrated. As a guide to such a course no better book could be desired than the ' Introduction to Inorganic Chemistry,' written by the late Professor W. A. Miller, and this has been hitherto the text-book of the junior classes under my charge.

The molecular theory has been adopted in a somewhat rigid form, not by reason of any special convictions of my own regarding its permanence as a scientific truth, but because I am satisfied by long experience that, whatever form it may ultimately assume, it is even now a most im- portant and almost indispensable aid to teaching chemistry.

I cannot conclude without expressing my thanks to several scientific friends, who have in the kindest manner examined my manuscript and have favoured me with valuable suggestions and encouragement.

I have, of course, not hesitated to avail myself of the

stores of information contained in Watts' most valuable Dictionary.

The exercises are for the most part culled either from examination papers given at Oxford, Cambridge, or London, or are taken from memoirs published in the journals of the various scientific societies. Many also are original.

W. A. T.

CLIFTON : *May* 1876.

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METRIC WEIGHTS AND MEASURES.

PREFIXES.—Myria-   ..   ..   10,000.
          Kilo-   ..   ..   1000.
          Hecto-   ..   ..   100.
          Deka-   ..   ..   10.
          (   )   ..   ..   1.
          Deci-   ..   .. $\frac{1}{10}$
          Centi-   ..   .. $\frac{1}{100}$
          Milli-   ..   .. $\frac{1}{1000}$

Inserting after the hyphen and in the brackets—
 (1.) *Metre*, gives the measures of length.
 (2.) *Litre*,   ,,   ,,   capacity.
 (3.) *Gram*,   ,,   ,,   weight.

LENGTH.

1 METRE = 10 decimetres.   (10 dcm.)
         = 100 centimetres.   (100 cm.)
         = 1000 millimetres.   (1000 mm.)
1000 Metres= 1 *Kilometre*.

CAPACITY.

1 LITRE   = 1 cubic decimetre.   (1 c.dcm.)
        = 1000 cubic centimetres.   (1000 c.c.)

WEIGHT.

1 GRAM or the weight of 1 c.c. of pure water at 4°C.
        = 10 decigrams.   (10 dg.)
        = 100 centigrams   (100 cg.)
        = 1000 milligrams.   (1000 mg.)
1000 Grams= 1 *Kilogram*.

ENGLISH EQUIVALENTS.

	NEARLY.	ACCURATELY.
1 METRE	= 3 feet $3\frac{3}{8}$ inches or $39\frac{3}{8}$ inches.	= $39 \cdot 37_{079}$ inches.
1 KILOMETRE	= 1100 yards	= $1093 \cdot 63_{31}$ yards.
1 LITRE	= $1\frac{3}{4}$ Impl. pint or 35 ounces.	= $1 \cdot 76_{0773416}$ pint.
1 GRAM	= $15\frac{1}{2}$ grains	= $15 \cdot 43_{23488}$ grains
1 KILOGRAM	= $2\frac{1}{6}$ pounds	= $2 \cdot 20_{46213}$ pounds

MEMORANDA.

Weight of 1 litre of hydrogen (at 0°C. and under 760 mm. bar.
   pressure)   = $\cdot 0896$ gram, or 1 crith.
Therefore 1 gram of hydrogen measures 11·16 litres.

Specific gravity of Hydrogen (Air = 1) = $\cdot 0693$.
    ,,   ,,   ,, Air   (H = 1)   = 14·42.

$$\therefore \; 1°C. = \tfrac{9}{5}°F. \text{ and } 1°F. = \tfrac{5}{9}°C.$$

To convert C. into F. temperatures $\dfrac{C \times 9}{5} + 32 = F.$

To convert F. into C. temperatures $\dfrac{(F - 32)5}{9} = C.$

SECTION I.

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CHAPTER I.

THE CONSTITUTION OF MATTER.

In order to facilitate the explanation of chemical phenomena, modern philosophers have found it convenient to
revive, in a somewhat modified form, the ancient hypothesis
that all bodies possessing extension and weight are made
up of stuff, substance, or *matter*, which is not uniform and
continuous throughout, but consists of separate very small
portions. Each of these small masses, which are called
molecules, is supposed to be to a certain extent independent
of the rest and isolated from them. The hypothesis further
requires us to suppose that the molecules constituting any
given species of matter are all alike, in size, weight, and
properties, and differ in these respects from other molecules.
Thus the molecules contained in one drop of water are
conceived to be precisely like the molecules in any other
drop of the same liquid. Similarly the molecules in a given
globule of the liquid metal mercury, or quicksilver, must be
assumed to be like all other molecules of the same metal; but
water molecules and mercury molecules differ altogether from
each other in weight and chemical properties. It must be
distinctly understood that molecules cannot be seen, and all
the arguments upon which the assumption of their existence
is founded, are derived from the examination of masses
of appreciable magnitude. We know nothing of isolated
individual molecules; the examination of these would be

for obvious reasons impossible, and even if such a division were actually possible, the condition or properties of a single molecule would be in no way comparable with those of a mass of matter in which many molecules are imagined to be naturally aggregated by cohesion or otherwise. But we may assume that when one kind of matter affects chemically another kind, the smallest quantity of each which is capable of entering into the reaction consists of a determinate number of molecules. For the purposes contemplated in this book, then, a molecule may be defined as the unit of chemical action ; that is, the smallest quantity which is able to take part in or result from a chemical change.

The constituent parts of molecules* are called *atoms.*† These may be regarded as the primordial masses of which molecules are supposed to be built up. The atoms consti- tuting a molecule must in some cases be assumed to be alike. The body made up of such molecules is called an element. Most commonly, however, there are reasons for considering that the atoms composing a given molecule are dissimilar, and then the body is a compound. The number of atoms in a molecule is very variable. A few elements have molecules which are assumed to consist of one atom only, others of two, three, or four ; whilst in compound bodies the number may amount to hundreds.

Chemistry is concerned chiefly with the investigation of those changes in properties which result from alterations in the internal constitution of molecules ; whilst the study of those forces which affect entire molecules, and masses of molecules without regard to their composition, belongs to the domain of Physics.

The materials which compose the earth's crust with its ocean and atmosphere and their inhabitants, may be roughly classified according to their mechanical condition into *solids* and *fluids.* Fluids are either liquids or gases.

* Molecule, diminutive, from Lat. *moles*, a mass.
† Atom, from ἁ, not, and τεμνώ, I cut.

A solid retains its form unless acted upon by pressure, by division with cutting instruments, by heat, or by solvents. Many solid bodies under suitable conditions assume definite geometric figures, which are generally bounded by plane faces, and thus give rise to crystals. This rigidity, by which the external form and relative position of parts is maintained, is due to what is called " cohesion." We should not, however, be justified in assuming that the constituent particles of solids are in a condition of absolute repose. Alteration of temperature and volume produced by the application of heat are attributable, according to the molecular theory, to the motion of the molecules, this motion being supposed to consist mainly in their rotation, or oscillation, or revolution, within a determinate space.

A liquid is recognised by its mobility, and by always assuming when at rest a horizontal level surface, except just where it comes into contact with the vessel containing it. The several parts of a mass of liquid are not held together with the same amount of force that binds together the parts of a solid, but that liquids are not altogether destitute of cohesion is shown by the spheroidal form of the rain drop, or of water sprinkled upon a greasy surface. The volume of a liquid is scarcely affected appreciably by pressure, even when very great, and pressure communicated to any one part of a mass of liquid is transmitted almost instantly and without loss to every other part.

From the phenomena of liquid diffusion which will be alluded to further on, it seems probable that the molecules of liquids move constantly from one part of the mass to another. These motions, however, are sluggish in comparison with the corresponding intestine movement which is observed in gases, and this is perhaps to be explained, at least in part, by the assumption that the molecules of liquids may be comparatively close together, so that their free motion is impeded by frequent collision.

Gases differ from solids and liquids in the circumstance

that they seem to be entirely discharged from the influence of cohesion. A mass of gas exhibits no surface, like that of a liquid, and no gas can be confined in a vessel which does not enclose it on every side.

The volume of a gas increases as the pressure upon it decreases (Law of Boyle), until when the pressure is nothing the bulk of the gas becomes greater than the capacity of any conceivable vessel. If, therefore, a small quantity of a gas be introduced into any part of a vacuous space, it immediately spreads itself out and pervades every portion of that space equally.

Solids, liquids, and gases alike expand upon the application of heat, but whereas each solid and liquid increases by a fraction of its volume which is peculiar to itself, all gases expand to practically the same extent by equal increment of temperature. In other words, whilst the co-efficients of expansion of solids and liquids are all different, those of true gases are the same in every case.

On the hypothesis that a gas, like a solid or a liquid, is a congeries of small masses or molecules, there are reasons for supposing that the molecules of gases are in constant and very rapid motion from place to place, and that they move in straight lines. A given molecule, however, cannot be supposed to pursue an uninterrupted course for any appreciable distance, but probably takes a new direction on the approach of another molecule.

These motions of translation which, in accordance with received views, have been here attributed to the molecules of gases and liquids, are directly related to the amount of heat which has been expended in producing the liquid from a solid, or the gas from a liquid. In other words, when heat is consumed in melting a solid, or in gasifying a liquid, it is necessary to admit that the vibratory motion to which the temperature of the heating agent is supposed to be due being communicated to the molecules of the object, may cause them not only to vibrate, but to move from place to

place ; and this altered motion corresponds with change of state.

For the further discussion of these speculations the reader must consult works on physics.* He will do well, however, constantly to set before his mind the fact that we possess at present no direct or positive proof even that molecules exist ; still less have we any evidence regarding the conditions under which they may subsist in mass. The molecular hypothesis, however, is no longer in the position which it formerly held as a relic of the vague speculative philosophy of the ancients. It has been raised to the rank of a theory which bids fair to rival in completeness and importance the Newtonian theory of gravitation itself. In neither case does the theory admit of direct experimental proof ; but both are accepted because they accord fully with the results of observation. The theory of molecules once admitted, all the recognised laws of chemical combination by weight and volume follow as necessary consequences. At the same time the phenomena connected with the physical properties of gases and liquids, such as the transmission of pressure and the remarkable laws of diffusion, find a rational and intelligible explanation such as no other hypothesis yet put forward has been competent to furnish. It is in fact not too much to assert that the rapid progress of modern chemistry and the intimate connection which it has been shown to have with other branches of physical science, as well as the illustrations it affords of the great doctrine of energy, are largely attributable to the general acceptance of this hypothesis. The science as it now stands may be regarded as a practical development of the molecular theory.

* The mathematical investigations of Krönig and Clausius, and of Rankine and Clerk Maxwell, have led to the establishment of the dynamical theory of gases, and have given a powerful impetus to the general recognition of the molecular theory by physicists. The student is recommended to make himself acquainted with the discussion of the subject from this point of view, which is given in Clerk Maxwell's " Theory of Heat."

When a solid is transformed into a liquid, or a liquid into a gas, an apparently abrupt change of physical properties occurs, and heat is abundantly absorbed without producing elevation of temperature. But the transition from one state to another is by no means so sudden as appears from the consideration of cases like that of water. Many solids, such as iron, pass through an intermediate state, in which they are more or less plastic or viscid before they finally assume the liquid condition ; and even the most perfect liquids with which we are acquainted are far from being absolutely mobile. Ether and alcohol, for example, flow more easily than water ; but even these liquids exhibit a certain degree of viscosity.

Experiments commenced in 1822 by Caignard de la Tour, and since continued and extended by Dr. Andrews, have shown that matter is capable of existing in a somewhat analogous condition intermediate between the liquid and gaseous states :—" By partially liquefying carbonic acid gas by pressure and then raising the temperature to 88° F., the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits, when the pressure is suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° F., no apparent liquefaction or separation into two distinct forms of matter could be effected even when a pressure of three or four hundred atmospheres was applied." (Andrews.) Nitrous oxide and sulphurous oxide, and other gases, give similar results. The striæ referred to are most probably the result of changes in density, caused by slight changes of temperature or pressure, as in ordinary liquids or gases when heated.

It thus appears that the various physical states of matter merge one into another by imperceptible gradations ; and if we adopt the molecular theory we can see some explanation of this. The change of a solid into a liquid, and of a liquid into a gas, ·is the result of alteration, generally increase, in the distances between the molecules. It is clear that in passing, for example, from the relative positions corresponding with the liquid state into those belonging to the gas the molecules must occupy successive intervening spaces. In doing this they must occupy successively an infinite number of different positions which may give rise to an infinite number of temporary modifications in the physical condition of the body.

CHAPTER II.

FUSION AND SOLUTION.

Fusion of Solids.—When, by the application of heat, a dry solid, such as sulphur or lead, is made to assume the liquid state, it is said to melt or undergo fusion. But when sugar is placed in water, it disappears, and is said to dissolve, and the liquid which results from such combination is called a solution. This distinction in terms is necessary, if only for practical convenience.

Amongst the elements the temperatures at which fusion occurs are very diverse, and there are but few cases in which any relation can be traced between this property and the chemical or other characteristics of the body. But among the compounds of carbon, which are very numerous, the determination of the melting point often serves as a convenient test whereby to distinguish two similar bodies from one another or to complete the identification of some substance under examination. As a general rule, it may, perhaps, be said that in a series of similar bodies those of smallest molecular weight melt at the lowest temperatures, as in the following examples :—

	Melting Point.	Molecular Weight.
Sulphur	115°	$_{n}32$
Selenion	217°	$_{n}79^{.}5$
Tellurium	about 500°	$_{n}128$
Formic acid	0°	46
Acetic acid	17°	60
Palmitic acid	62°	256
Stearic acid	$69^{.}2$	284
Cerotic acid	78°	410
Melissic acid	88°	452

There are, however, numerous exceptions to this rule. One example will suffice :—

	Melting Point.	Molecular Weight.
Cadmium	$315°$	112
Zinc	$423°$	65
Magnesium	low red heat	24

In very many cases a mixture of two or more substances melts at a lower temperature than either of the ingredients.

Mixtures of the fatty and other acids melt at lower temperatures than the pure acids ; the carbonates of potassium and sodium melt more easily when mixed than when alone ; an alloy of potassium and sodium is liquid at the ordinary temperature ; and an alloy of cadmium, tin, lead, and bismuth melts in hot water.

Solution of Solids.—The extent to which solid bodies are dissolved by liquids exhibits still greater diversity, and it is possible to generalise still less with regard to this property than when referring to the phenomena of fusion.

The most general fact that has been observed is, that solubility increases with rise of temperature ; or, in other words, a hot liquid dissolves a given solid more freely than the same liquid when cold. But although this statement is true of a very large number of soluble bodies, it is subject to some well-marked exceptions. Thus, common salt dissolves to very nearly the same extent in cold as in boiling water, and lime, calcium sulphate, barium acetate, and other salts are very decidedly less soluble in hot water than in cold.

Liquids, too, are observed to exercise a certain selection in the solids they take up. Thus, water dissolves a vast number of salts, which, in the majority of cases, are insoluble, or nearly so, in alcohol. On the other hand, alcohol dissolves a great many carbonaceous substances, such as organic bases, resins, and camphor, which are almost un_ affected by water. And, without straining the idea too far, it is not too much to say that there is in many cases a rela-

tion observable between the chemical composition of the
solvent and that of the solid it dissolves. Ether and benzene,
both highly carbonaceous liquids, dissolve freely fats and
other substances which are rich in carbon ; carbon bisul-
phide is the best solvent for the common form of sulphur ;
phosphorus trichloride dissolves phosphorus. This relation
cannot, however, be said to be general, and at present we
possess no clue to the laws which regulate the solution of
solids in liquids. It does appear, however, that the union
between a liquid and the substance in solution resembles
more or less closely the act of chemical combination. One
reason for so regarding it is supplied by the thermal changes
that accompany solution.

In the process of dissolving many solids, there is a very
considerable reduction of temperature consequent upon
the change of state which the solid undergoes, its lique-
faction necessarily rendering a certain amount of heat
latent. Freezing mixtures are often made on this principle.
But in not a few other cases the temperature rises in a very
marked degree. This is due to the heat generated by the
combination of the solid with the liquid in which it is im-
mersed, and is sufficient not only to satisfy the requirements
of the change of condition which the solid undergoes in
becoming a liquid, but also to raise the temperature of the
resulting liquid. It has also been observed that some solu-
tions, when further diluted with the same liquid, develop suc-
cessive though smaller quantities of heat. It seems fair to
attribute these continuous manifestations of heat to the
process of aggregation of molecules under the influence of
chemical attraction. This is in accordance with the very
generally observed, though not universal, fact that chemical
combination is attended by liberation of heat.

Sulphuric acid furnishes an instance of the kind referred
to.

Relative quantities of heat evolved·by mixing sulphuric acid with successive quantities of water.						
One molecule of sulphuric acid						
with 1 mol. of water .	.	.	.	.	.	69·7
2 mols.	,,	.	.	.	.	33·7
3 mols.	,,	.	.	.	.	15·4
4 mols.	,,	.	.	.	.	12·9
5 mols.	,,	.	.	.	.	9·0
6 mols.	,,	.	.	.	.	7·3
&c.						&c.
120 mols.	,,	.	.	.	.	0·

Some interesting facts bearing on this question have lately been discovered by Professor Guthrie, who finds that all salts are capable of combining with definite quantities of water when their solutions are exposed to a sufficiently low temperature. And from the fact that the bodies thus obtained present a constant melting and solidifying point, a distinct crystalline form and other well-marked characteristics, it seems not unfair to regard them as true chemical compounds. Ammonium chloride, for example, is, under ordinary circumstances, an anhydrous salt ; but when the temperature of its aqueous solution is reduced to $- 15°$, a crystalline body is formed in which one molecule of the ammonium chloride is united to twelve molecules of water. In other cases these " cryohydrates," as they have been called, contain a much larger proportion, amounting to hundreds of molecules, of water. The process of solution of a solid body, then, would appear to consist in the combination of the body, in the first instance, with a certain limited, though relatively large quantity of the solvent forming a hydrate, which at ordinary temperatures above $0°$ is a liquid, and this liquid then mixes with the rest of the solvent by the ordinary process of diffusion.

Naturally connected with the production of solutions is the process of crystallisation, as it is in the gradual passage from the liquid to the solid state that we find the most generally useful method for the formation of crystals.

The crystallisation of a crystallisable solid from its solutions occurs when the percentage of solid present in the liquid exceeds a certain limit dependent on the nature both of the solid and the liquid in which it is dissolved. This condition may be brought about either by allowing part of the solvent to evaporate, or by altering, in general by lowering the temperature. Crystals are then formed, and these crystals, in the majority of cases, contain not only the elements of the dis-solved substance, but a portion of the solvent united to it in definite molecular proportions. This is particularly noticeable in the case of aqueous solutions, and the water thus combined is spoken of as *water of crystallisation.* Alcohol and benzene, and probably other liquids, unite with salts and other crystallisable bodies in the same manner. It is note-worthy that the proportion of water of crystallisation is principally dependent upon the temperature at which the process of crystallisation takes place. Thus, sulphate of sodium crystallises from water at temperatures above 40° C. in the anhydrous state. But at the ordinary temperature of the air, the solution deposits crystals which contain ten molecules of water with one molecule of the salt, whilst at — 7°, the crystals formed contain 166 molecules of water. (Guthrie.)

Water of crystallisation is always expelled from a salt by exposure in a vacuum, or at the temperature of boiling water. The water which is given off by many bodies at higher temperatures is supposed not to exist as such in the compound, but to be produced in consequence of decom-position. Some compounds, however, evolve at ordinary temperatures, a vapour of appreciable tension, and these soon lose a part or the whole of their water of crystallisation, at the same time crumbling away to a shapeless mass. Such salts are said to be *efflorescent.* On the other hand, certain dry solids, such as potassium hydrate, and carbonate, cal-cium chloride, and chromium trioxide, have the power of condensing and combining with vapour of water so freely,

that when exposed to the atmosphere, or to any gas containing moisture, they rapidly liquefy in the water which they thus absorb. Bodies of this kind are said to be *deliquescent.*

Solution of Gases.—All gases dissolve to a greater or less extent in water, but, unlike solids, their solubility diminishes as the temperature rises, so that in most cases* the dissolved gas may be completely expelled from a liquid by boiling, whilst the amount taken up may be greatly increased by cooling the liquid.

Increase of pressure also augments the solubility of gases in a direct ratio. It is therefore necessary in making any statement as to the solubility of a gas to observe the conditions of temperature and pressure under which that solubility was estimated. The following examples will serve to show how greatly gases differ in the extent to which they dissolve in water.

At $0°$ C, and under a pressure of $760°$ mm. barom.

1 volume of water will dissolve

Hydrogen	·0193
Nitrogen	·02035
Oxygen	·04114
Nitrous Oxide	1·3052
Carbon Dioxide	1·7967
Hydrogen Sulphide	4·3706
Sulphur Dioxide	79·789
Ammonia	1148·8

The numbers given above represent volumes of the several gases measured at $0°$ and 760 mm., and constitute the *co-efficients of absorption* of these gases at that particular temperature and pressure.

The general statement that the weight of a gas dissolved by a liquid is directly proportionate to the pressure is often known as the law of Henry and Dalton. It admits of another expression ; for since, according to the law of Boyle,

* Exceptions occur in the cases of hydrochloric acid and some other gases.

the volume of a gas diminishes as the pressure upon it increases, it is obvious that the volume of gas thus held in solution must always be the same, whatever the pressure.

These rules no longer hold good when the gas and the liquid exert a chemical action upon each other, and exceptions must also be recognised in the case of the more soluble gases, such as hydrochloric acid and ammonia.

The determination of the absorption of gases by liquids may be applied in certain cases to the elucidation of some important theoretical and practical questions. Atmospheric air furnishes an example which will be worth the consideration of the student.

When a mixture of gases is exposed to the action of a solvent, the quantity of each of the constituents dissolved by the liquid will depend first upon its co-efficient of solubility, and secondly upon the proportion in which it exists in the mixture. This proportion determines the pressure which each gas present exerts upon the surface of the liquid, and consequently regulates the amount of it which is dissolved. The total pressure produced by the mixture is therefore the sum of those partial pressures due separately to the individual constituents. To make this more clear :

Suppose a very large vessel containing a very little water, and filled with oxygen, under a pressure of one atmosphere. It is plain that if four-fifths of the gas were removed the pressure would be reduced to one-fifth of an atmosphere, and the quantity of oxygen dissolved would be only one-fifth the quantity taken up under the previous conditions, provided, of course, that the temperature remain constant. An exactly similar vessel can be conceived filled with nitrogen under one atmosphere, and containing a little water. If one-fifth of the nitrogen were removed, the pressure of the remainder would be only four-fifths of an atmosphere, and the quantity dissolved would be reduced to four-fifths. Lastly, a similar vessel, filled with atmospheric

air, contains a gas in which the conditions of the two previously supposed experiments are combined.

Air is composed very nearly of four volumes of nitrogen to one volume of oxygen, and by reason of the greater solubility of oxygen the proportion of the two gases one to the other is found to be disturbed when air is shaken up with water, the dissolved gas being richer in oxygen, the residual air richer in nitrogen, than the original.

No stronger evidence could be adduced in favour of the view generally held, that in atmospheric air the two main components are not united chemically, but are in a state of intimate mechanical mixture.

Note.—The following is an example of the kind of problem that might occur in connexion with this subject :

Calculate the percentage composition of the gas which would be dissolved by water exposed in a room full of air containing 79 N, 20·6 O, and ·4 of CO_2 in 100 volumes (temp. 0° and bar. 760 mm.).

> Coeff. of sol. for oxygen .   .   .   ·04
> „   „   nitrogen   .   .   ·02
> „   „   carbondioxide   .   1·79

The pressures are proportional to the volumes of the gases present. Therefore the relative quantities dissolved would be :

Nitrogen	79	×	.02	=	1·58
Oxygen	20·6	×	·04	=	·824
Carbondioxide	·4	×	1·79	=	·716

The total quantity   .   .   . =   3·120

The percentage composition of the dissolved gas would therefore be :

> Nitrogen   .   .   .   .   .   . 50·6
> Oxygen   .   .   .   .   .   . 26·4
> Carbonic dioxide .   .   .   .   . 22·9

CHAPTER III.

LIQUID DIFFUSION AND DIALYSIS.

An aqueous solution of sugar or of salt is heavier than water, and may be readily poured through a funnel with a long stem, into a glass of water in such a way as to form a separate stratum at the bottom. If the solution is coloured, it will soon be noticed that the colour gradually extends upwards through the liquid, until, after a few hours or a few days, according to circumstances, the whole liquid is uniformly tinged. But it is not necessary that the liquid should be coloured. The taste, specific gravity, refractive power, or the application of chemical tests, will soon give indications that the solution from below is mixing with the liquid above. This process of spontaneous intermixture is called diffusion. It results from the proper motion of the molecules of the liquid, and cannot be referred to the disturbing influences of changes of temperature. The rapidity with which diffusion of this kind takes place, and the limit of its action, depend very much upon the nature of the liquids employed.

The power of interdiffusion is by no means universal among liquids, some liquids being, like mercury, oil, and water, quite incapable of mixing together under any circumstances; whilst others, such as water and solution of hydrochloric acid, mingle spontaneously in consequence of very rapid diffusion. We are indebted for nearly all the information we possess on this subject to the late Professor Graham. His experiments were conducted very nearly in the manner already described at the beginning of the chapter. The glass vessel in which diffusion was allowed to go on was graduated into equal divisions, from the bottom upwards; and after the introduction of the two liquids, the whole was left in a room, the temperature of which was kept as uniform as possible.

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After a time, the liquid occupying successive divisions of the vessel, was removed by a small syphon, or pipette, and analysed, in order to ascertain the extent to which diffusion had taken place. In this way a number of conclusions were arrived at, amongst which the following are the most important :—

1. Bodies are divisible, as regards their diffusive power, into two classes. Those which diffuse most readily through a given liquid menstruum are, for the most part, crystallisable substances, and are termed by Graham *crystalloids* ; whilst the least diffusible bodies are uncrystallisable with, in most cases, high molecular weight, and are denominated *colloids*,* from their resemblance to glue, which may be taken as the type of this class. The following list supplies the *times* of equal diffusion by the substances there named ; and it will be seen that albumen and caramel, both of which are uncrystallisable substances of somewhat indefinite composition, are far behind the rest :—

Hydrochloric acid	1
Chloride of sodium . . .	2·33
Sugar	7
Sulphate of magnesium . . .	7
Albumen	49
Caramel	98

Thus hydrochloric acid diffuses more than twice as rapidly as chloride of sodium, seven times as rapidly as sugar or magnesium sulphate, forty-nine times as rapidly as albumen, and nearly one hundred times as rapidly as caramel. Hydrochloric acid is one of the most diffusive substances known.

2. Equal rates of diffusion are exhibited in many cases by the members of isomorphous groups. Thus hydrochloric, hydrobromic, and hydriodic acids have nearly the same

* κόλλα, glue.

diffusion rate ; so also have the chlorides, bromides, and iodides of the alkali metals ; the nitrates of barium, strontium, and calcium, and the sulphates of magnesium and zinc.

3. The rate of diffusion increases with the temperature, and when the solution is not too concentrated, is proportional to the strength of the solution.

By taking advantage of this difference in diffusibility, mixed salts may be separated from one another to a certain extent, and crystalloids may be isolated pretty perfectly from admixture with colloids. In the practical application of this process, it has been found convenient to separate the liquids undergoing diffusion by some membrane or partition composed of colloid material, and this mode of diffusion, through a septum, is called *dialysis*. The process is a very simple one. The liquid holding in solution a mixture of crystalloids and colloids is placed in a sort of tray or sieve, formed of a sheet of parchment paper stretched over a hoop. This vessel, which is called the *dialyser*, is made to float in a dish of pure water, which, after a time, can be renewed if necessary. Under these circumstances, the crystalloids pass out by diffusion through the membrane (which must be perfectly free from holes), and by evaporating the liquid down may be obtained in a condition of tolerable purity.

The application of this method led to the discovery of the soluble colloidal forms of ferric hydrate, silicic acid, alumina, and other bodies which had been previously known only in the pectous or gelatinoid condition, and the study of which could not fail to throw considerable light on the obscure natural processes by which these bodies are deposited as minerals in the crystalline form, and in a great state of purity. If, for example, we take a solution of silicate of sodium, and add to it a slight excess of hydrochloric acid, we obtain a perfectly clear liquid, which contains the very substance referred to above as colloid silicic

acid ; but in this liquid it is mixed with the acid used and the common salt formed by the decomposition. The process of dialysis furnishes the means of separating these latter substances without causing the precipitation or other alteration of the silicic acid, which is left on the dialyser in the form of a colourless limpid solution. This solution is, however, very unstable, especially when concentrated, and the addition of even very minute quantities of various salts causes the whole of the silica to separate out in the form of a translucent jelly, which cannot be re-dissolved, except by the addition of a fresh quantity of alkali.

Liquid stannic, titanic, tungstic, and molybdic acids have been prepared by a similar process.

The ultimate pectisation of liquid silicic acid and other colloids is preceded by a gradual thickening of the liquid, and just before gelatinising silicic acid flows like an oil. These effects are doubtless the result of the tendency of the particles of colloids to cohere, aggregate, and contract. This tendency manifests itself occasionally in the exercise of very considerable force. Thus the contraction of gelatine drying in a glass dish over sulphuric acid, together with the adhesion of the gelatine to the glass, is said to be sufficiently powerful to tear up the surface of the glass. Glass is itself a colloid, and the permanent adhesion between the surfaces of polished plates of glass is a well-known circumstance, which is referred by Graham to this class of phenomena.

CHAPTER IV.

EVAPORATION AND EBULLITION.

A LIQUID boils when, by raising its temperature, the elasticity of the vapour formed at any point in the liquid is capable of overcoming the pressure at that point. This pressure is made up of the pressure of the atmosphere and that of the superincumbent stratum of liquid. In a vessel of inappreciable depth, and when the mercurial column in the barometer is 760 mm. high, alcohol boils at $78°\cdot4$ and water at $100°$.

The tension of alcohol vapour is, therefore, at any temperature below its boiling-point, greater than that of water, and alcohol is said to be more *volatile* than water. Nearly all liquids are volatile, but the temperatures at which they evaporate freely are very diverse. There is, for example, a wide range between the volatility of ether and of molten silver, or between that of liquid carbon dioxide and of metallic mercury.

The observation of the boiling point of liquids is an operation of daily occurrence in the laboratory, and although very few general laws connecting the boiling point with chemical characters have been traced out, a few general observations have been made, to which the attention of the student must be directed. The conversion of a liquid into a gas or vapour is attended by the absorption of heat, and this heat is consumed in giving to the molecules of the liquid a new and more rapid motion. From this consideration it would appear that bodies formed of light molecules would be more easily vaporised than others constituted of complex and consequently heavy molecules. Such is indeed the case, and, in the broadest sense, such a statement would be nearly true. But when we examine

individual cases, we meet with so many exceptions and
anomalies, that it is obvious such a law must be applied
with extreme caution. It is, however, permissible to say
that bodies which are strictly comparable in regard to
chemical and other physical qualities do in nearly all cases
exhibit the relation referred to. Among the elements the
most noteworthy instances are the following :—

	Molecular Weight.	Boiling Point.
Chlorine . . .	71	$-50°$
Bromine . . .	·160	$63°$
Iodine . . .	254	$175°$
Oxygen . . .	32	permanently gaseous
Sulphur . . .	64 ?	$440°$
Selenion . .	159 ?	below a red heat
Tellurium . .	258 ?	white heat
Nitrogen . .	28	permanently gaseous
Phosphorus . .	124	$290°$
Arsenic . . .	300	volatilises at red heat without fusion
Antimony . .	244 ?	white heat
Bismuth . . .	420 ?	white heat

Groups of similarly constituted compounds show the
same relations.

	Molecular Weight.	Boiling Point.
Sulphur Dioxide	64	$-10°$
Sulphur Trioxide	80	$46°$

But the most important cases are observable among the
carbon compounds, which form *homologous* series, to which
reference will be made hereafter. One example will suffice
in this place. The following compounds all contain carbon
and hydrogen in proportions which may be represented by
the general formula C_nH_{2n+2} :—

	Molecular Weight.	Boiling Point.
Methane (marsh gas)	16	gaseous
Ethane . . .	30	gaseous
Propane . . .	44	gaseous
Tetrane . . .	58	1°
Pentane . . .	72	38°
Hexane . . .	86	70°
Heptane . . .	100	99°
Octane . . .	114	124°
	&c.	&c.

In this series, for every increase of 14 on the molecular weight, the boiling point rises by about 30° to 35°.

In the determination of boiling points it is usual to observe, by an accurate thermometer, the temperature of the vapour evolved by the boiling liquid, and not that of the liquid itself. This precaution is necessary when glass vessels are, as usual, employed, in consequence of a peculiar adhesive attraction which glass exercises, and which causes the boiling point to be slightly raised above the true temperature of ebullition. This adhesion sometimes gives rise to the phenomenon of irregular ebullition or " bumping." The entire thread of mercury in the thermometer should be immersed in the vapour, so as to be heated by it, and the height of the barometer should be noted at the time of the experiment.

This last is a precaution which is very generally neglected, and its neglect is probably the cause of some of the discrepancies noticed between calculated and observed boiling points and between the results of different experiments.

The determination of the boiling point is often useful in deciding as to whether a given liquid is a mixture or a homogeneous body. When heat is applied to a mixture of volatile liquids the mixture begins to boil at a temperature very near to the boiling point of its most volatile constituent, and if the temperature is not allowed to rise above

this point, ebullition in most cases soon comes to an end. But if the application of heat is continued whilst the thermometer is kept in the vapour, the temperature may be observed to rise continuously till the whole of the liquid has boiled away. If this operation is conducted in a flask connected with a condensing apparatus and a receiver, and if the receiver is changed at intervals, so that the several portions which pass over between certain limits of temperature are received in separate vessels, a more or less complete separation of the constituents of the liquid may be effected. Such a process is called *fractional distillation*.

The compression of a vapour tends to produce the same change of state as lowering its temperature. In either case the approximation of the molecules is attended sooner or later by the liquefaction of a part of the vapour. With these facts in view, and considering the generally close resemblance between vapours and those bodies which are commonly called true gases, Faraday came to the conclusion that the latter are not essentially different from the former, but are in truth the vapours of volatile liquids far removed at ordinary temperatures from their boiling points. This conclusion he verified experimentally by enclosing in strong $\wedge$-shaped glass tubes materials capable of evolving the gases he wished to examine. On the application of a gentle heat to these materials gas was generated, and by its accumulation in the confined space, sufficient pressure was exerted to cause its partial liquefaction. In this way ammonia, chlorine, and other gases were reduced to the condition of limpid liquids, and by the combined use of pressure and low temperature, produced by powerful freezing mixtures, a great many other bodies, which till then had been known only in the gaseous form, were also liquefied. Larger apparatus constructed on the same principle as Faraday's glass tubes, were subsequently employed by different experimenters, and at the present time several gases, such as

carbonic anhydride and nitrous oxide, are liquefied on a large scale by compressing them by powerful force-pumps into iron cylindrical bottles fitted with stopcocks. By such methods all known gases have been, with six exceptions, reduced to the liquid state.

Those which refuse to liquefy, viz., oxygen, hydrogen, nitrogen, carbonic oxide, nitric oxide, and methane, are all gases of comparatively small density, though not less dense than some, *e.g.* steam and ammonia, which assume the liquid condition very readily.

There can be very little doubt, therefore, that these six gases would yield like the rest if a sufficiently great pressure, assisted by very low temperature, could be applied.

The evaporation of liquefied gases is attended by the absorption of much heat, and in some cases the reduction of temperature is such as to cause the solidification of part of the liquid. Carbonic anhydride can be obtained in the form of a white snow-like solid by allowing a fine stream of the liquefied gas to escape into the air. Part of it evaporates very rapidly, and so much heat is thus rendered latent that the remainder freezes.

The following table shows the amount of pressure in atmospheres necessary at the temperature of $0°$ to liquefy some of the more important of the liquefiable gases :—

PRESSURE IN ATMOSPHERES—TEMP. $0°$ C.

Sulphur dioxide	.	.	.	.	1·53
Cyanogen	.	.	.	.	2·37
Hydriodic acid	.	.	.	.	3·97
Ammonia	.	.	.	.	4·4
Chlorine	.	.	. about		5
Hydrogen sulphide		.	.	.	10
Nitrous oxide .	.	.	.	.	32
Carbon dioxide	.	.	.	.	38·5
Hydrochloric acid .		.	. about		42

Some of these may be liquefied by cold alone under the ordinary atmospheric pressure. Thus—

Sulphur dioxide condenses at	.			.	. $-10°$
Cyanogen .	.	.	,,	.	. $-22°$
Ammonia .	.	.	,,	.	. $-36°$
Chlorine .	.	.	,,	.	. $-50°$
Carbon dioxide .	.	.	,,	.	. $-87°$

On the other hand, Dr. Andrews has found that if the temperature be raised to a certain point, a gas which is otherwise liquefiable can no longer be liquefied by pressure, even when it amounts to several hundred atmospheres. This point, which varies with the nature of the gas operated upon, is called the *critical point*. In the case of carbon dioxide it is 31° C.

It has been already stated earlier in the chapter that if we compare together liquids which consist of the same elements, and which present the same general properties, those which have the simplest constitution are the most readily converted into vapour. The converse is equally true. Comparing together similarly constituted gases and vapours, we find that those which are composed of simple molecules are more difficult to liquefy by cold or compression than others of more complex constitution. These facts are sometimes serviceable in helping to decide questions as to the relative complexity of two nearly allied compounds. For example, there are two oxides of carbon, both gaseous at ordinary temperatures, but one of them capable of liquefaction under pressure. It follows that the liquefiable oxide is in all probability made up of heavier molecules than the other, and this view is supported by a comparison of the densities of the two gases. Carbonic anhydride gas, which is liquefiable, is bulk for bulk 1·57 times heavier than carbonic oxide.

Nitrous and nitric oxide, ethylene and marsh gas, furnish examples of the same kind.

CHAPTER V.

DIFFUSION AND DIALYSIS OF GASES.

A VERY remarkable property of gases and vapours is their power of mixing with one another, even in opposition to gravity.

If a bottle of any odorous gas is opened in any part of a room of constant temperature and free from draughts, the smell of the gas soon becomes perceptible in every part of the room, and, after the lapse of a short time, equally in every part. Notwithstanding that, as in the case of sulphuretted hydrogen, a heavy gas may be selected for the experiment, it would be easy to prove by anaylsis of the air that every part of it is equally impregnated with the foreign matter. Other experimental illustrations of the same law may easily be devised. A bottle of hydrogen held mouth downwards in the air for a short time soon becomes ex-plosible. A jar of air inverted over another filled with carbonic acid gas, soon acquires the power of giving, like carbonic acid, a precipitate with lime water. And this process of intermixture proceeds almost equally well if the gases are separated from each other by a partition formed of some porous material.

A thin plate of unglazed earthenware, a slice of artificially compressed graphite, or a cake of dry plaster of Paris, may be employed for the purpose. A very effective form of apparatus consists of a clay battery cell closed by a cork, through which a yard or so of glass tubing open at both ends is made to pass. By means of this simple apparatus it may be shown that different gases penetrate the porous clay with different degrees of rapidity, and that light gases effect a passage more quickly than heavier ones. The con-

sequence of this difference of diffusion-rate is that a
difference of pressure is established inside the cell, and if
the open end of the tube is dipped into water a certain
quantity of gas is expelled in bubbles from below, or the
liquid is forced by the atmospheric pressure up the tube.
If, for example, the clay vessel previously full of air is
surrounded by hydrogen gas, intermixture of the air within
and the hydrogen without takes place through the clay ; but
since the hydrogen diffuses more rapidly than the air, the
quantity of gas within is rapidly increased, and some of it
visibly finds its escape from the open end of the tube
through the water.

Early observations of and experiments upon gaseous
diffusion were made by Priestley in the last century, and
by Döbereiner in 1825 ; but Graham gave the explanation
of the phenomena, and by precise and long-continued
experiments established the law :

*The velocities of diffusion of different gases are inversely
proportional to the square roots of their densities.*

Graham's experiments were for the most part conducted
with a very simple apparatus, consisting of a straight wide
glass tube closed at its upper extremity by a disc of porous
stucco or graphite. This tube was filled with hydrogen or
other gas over the mercurial trough, the graphite plate being
covered during this operation with a sheet of gutta percha.
The mercury within the tube was kept at the same level as
the mercury in the trough, in order that there might be no
alteration of pressure whilst the diffusion was proceeding,
and at the same time the temperature and barometric
pressure were recorded. After the lapse of a certain
interval, measured by a chronometer, the volume and com-
position of the residual gas could be determined.

The following table embodies some of the results
obtained in this way, the pressure and temperature being
supposed to be the same in all cases :—

DIFFUSION OF GASES.

Name of Gas.	Density.	Square Root of Density.	$\frac{1}{\sqrt{Density.}}$	Velocity of Diffusion.
Air.	I	I	I	I
Hydrogen .	·0693	·2632	3·7794	3·83
Marsh gas .	·554	·774	1·3375	1·344
Carbonic oxide .	·9678	·9837	1·0165	1·0149
Nitrogen .	·9713	·9856	1·0147	1·0143
Oxygen .	1·1056	1·0515	·9510	·9487
Carbonic dioxide	1·529	1·2365	·8087	·812

It will be noticed that the observed rate of diffusion agrees very nearly with the rate calculated from the density of the gas, but in no case is there absolute concordance. This is, probably, in part due to the errors inevitable in any experimental investigation, especially where gases are concerned, but is also in some degree attributable to the fact that the diaphragm employed possesses an appreciable thickness, so that in passing through the pores the gas encounters considerable resistance.

By taking advantage of the unequal diffusibility of gases of different density, a partial separation of mixed gases may in some cases be effected.

The gases constituting atmospheric air, for example, may be, to some extent, separated from each other by causing a slow current of air to flow through a clay tube passing through a glass tube which has been exhausted as completely as possible by the air-pump. The nitrogen being lighter, and consequently more diffusible than the oxygen, passes more abundantly into the vacuous space, leaving the residual air richer in oxygen than it was originally.

The physical explanation of the phenomena of diffusion depends directly upon the mechanical theory of gases, which has been (Chap. I.) already discussed. The mole-cules of a gas are supposed to move constantly in straight

lines till they come nearly into contact with other moving molecules, or with the walls of the containing vessel. If these walls are perforated at intervals with apertures large enough to permit the passage of a molecule, we may con- ceive that although many molecules continue to rebound as though the surface were impervious, yet that a great many others may find their way into and through these short pas- sages, and so into the atmosphere beyond. Molecules from the external atmosphere may be assumed to pass inwards in precisely the same manner, and if the densities of the gases on the two sides of the partition are the same, the number of molecules passing inwards in a given time is exactly equal to the number passing outwards, and no change of volume or of pressure can result. But if the gases are of different densities, molecules of the lighter gas pass through more rapidly than those of the heavier, and a change is produced in the tension or elastic force of the gas enclosed in the porous vessel.

This pressure, exerted by a gas in opposition to that which it has to bear when enclosed in a vessel, is re- presented according to the dynamical theory as the result of the continuous showering down of its molecules upon the surfaces with which it is in contact. The mole- cules of different gases being of different weights, they must move with different degrees of velocity, the light molecules more rapidly than heavier ones, in order to pro- duce the same amount of pressure. Hence, when the gas in contact with the porous surface is a light gas, its mole- cules must be supposed to fall upon a given area more fre- quently than when the gas employed is heavier, and conse- quently the opportunities for the escape of molecules through the pores are more frequent. Hence it is that light gases diffuse more rapidly than heavy gases.

Gases have not only the power of passing by diffusion through porous substances, but under certain circumstances penetrate membranes, and even sheets of metal which are

absolutely destitute of pores. This phenomenon differs entirely from diffusion, for it is not found that the lightest gases traverse such substances most rapidly ; indeed, the contrary is more generally the case. Moreover, the metals which are so remarkable for their power of transmitting some gases are absolutely impermeable by others.

A few simple experiments will give the student an idea of the general character of the phenomena we are discussing. If a thin india-rubber balloon (such as are sold at the toy-shops), inflated with air, is immersed for a few minutes in a vessel full of carbonic dioxide gas, the balloon becomes largely distended, and if a band of tape is fastened round it before the experiment, it generally bursts after immersion in the gas for a short time. A similar balloon filled with hydrogen or carbonic dioxide gas quickly collapses when exposed to the air. Such a film of rubber appears to have no porosity, but rather to resemble a film of liquid in its relations to gases. The penetration of the rubber and similar colloids by a gas appears to be due to the absorption of the gas by one surface of the colloid and its transmission to the other surface by the agency of liquid and not gaseous diffusion. The liquefied gas then volatilises into the vacuum or atmosphere on the other side.

The passage of gases through metallic plates at a red heat is referred by Graham to a somewhat similar cause. Thus, at a red heat, both platinum and palladium, and even iron, are permeable by hydrogen gas ; and this is evidently connected with the fact that the same metals are capable of absorbing and retaining considerable quantities of hydrogen when that element is presented to them under suitable conditions. Thus a sheet of palladium connected with the negative pole of a battery, and immersed in acidulated water, becomes charged with upwards of 200 times its volume of hydrogen gas. The same metal in a spongy state absorbs 686 times its volume of hydrogen when heated in the gas to 200°. This " occlusion " of

hydrogen is not attended by any alteration in the appear-
ance of the metal, although its volume is increased, and
consequently its density diminished.

Other gases are occluded in a similar manner by other
metals ; but in each case a certain selective power is mani-
fested on the part of the metal.   Thus, platinum and pal-
ladium take up hydrogen freely, but no other gas to an
appreciable amount ; iron takes up hydrogen and carbonic
oxide, and melted silver absorbs oxygen.

CHAPTER VI.

RELATION OF GASES TO TEMPERATURE AND PRESSURE.

Law of Boyle.—" The volume of a given mass of any
gas varies inversely as the pressure."

Thus, if V is the volume when the pressure is P

The volume of the gas becomes

$\frac{1}{2}$ V when the pressure is .   .   2 P

$\frac{1}{3}$ V   ,,   ,,   ,,   ,,   .   3 P

$\frac{1}{4}$ V   ,,   ,,   ,,   ,,   .   4 P

$\frac{1}{n}$ V   ,,   ,,   ,,   ,,   .   n P

Also

2 V   ,,   ,,   ,,   ,,   . $\frac{1}{2}$ P

3 V   ,,   ,,   ,,   ,,   . $\frac{1}{3}$ P

n V   ,,   ,,   ,,   ,,   . $\frac{1}{n}$ P

Hence the pressure which is produced by the *elastic force*
or *tension* of a gas is proportional to its density.

So that if *pressure* increases,
density increases,
and *volume* diminishes.
Also if *volume* increases,
pressure and *density* diminish.

Boyle's law is not absolutely obeyed by any known gas ; but hydrogen and the other incondensable gases conform to it very nearly, and thus present the nearest approach to the condition of a perfect gas with which we are acquainted. With change of pressure the liquefiable gases and vapours increase or decrease in volume to a greater extent than permanent gases.

The pressure and density of atmospheric air, and of gases which are in communication with it, are estimated by the aid of the barometer. This instrument, in its simplest form, consists of a straight glass tube, somewhat less than a metre long, and closed at one end. The tube is filled with pure mercury, free from air, and then inverted with the open end beneath the surface of pure mercury. The liquid metal then falls from the closed extremity, leaving a space which is generally referred to as the " Torricellian vacuum." It contains nothing but mercurial vapour. It is usual to consider that the atmosphere possesses its average and normal density when, at the sea level and at the temperature of o° C, the column of mercury sustained by the atmospheric pressure is 760 millimetres (or 29·92 inches) high, measuring from the surface of the mercury in the reservoir to the surface of the mercury within the tube. This amount of pressure is often spoken of as one *atmosphere.*

In accordance with the law of Boyle, the volume of a gas under altered barometric pressure, can be calculated by the formula :

$$\frac{V}{V_1} = \frac{P_1}{P}$$

in which V is the given volume under pressure P, and V_1 is the new volume when the pressure is altered to P_1. So that

$$V_1 = \frac{V}{P_1} \times P.$$

Example.—100 volumes of air are measured off when

the barometric pressure is 740 mm.; what will be the volume of the same air when the barometer stands at 760 mm. ?

$$\text{Here } V = 100, \, P = 740, \, P_1 = 760.$$
$$\text{Then } V_1 = \frac{100 \times 740}{760} = 97\cdot3 \text{ vols.}$$

Answer.

LAW OF GAY-LUSSAC AND CHARLES.

Air expands by $\dfrac{1}{273}$ of its volume at 0° for every increase in temperature of 1° C.

Thus 273 volumes of air at			.	.	0°
Become 274	,,	,,	.	.	1°
275	,,	,,	.	.	2°
276	,,	.,	.	.	3°
$273 + t$,,		,,	.	.	t°
Also 273	,,	,,	.	.	0°
Become 272	,,	,,	.	.	-1°
271	,,	,,	.	.	-2°
270	,,	,,	.	.	-3°
$273 - t$,,		,,	.	.	$-t^\circ$

And generally $273 + t$ at t° become $273 + T$ at T°.

This fraction $\dfrac{1}{273}$ or $\cdot003665$, is called the co-efficient of expansion, and represents almost exactly the increment or decrement which occurs in a measured volume of air or other permanent gas for every change of temperature of one degree centigrade, provided the pressure remains unchanged. The co-efficient of all gases is *very nearly* coincident with that of air, and for chemical purposes may, without inconvenience, be assumed to be the same. Strictly speaking, however, every gas has a co-efficient of its own, which, in the case of the liquefiable gases, is perceptibly

greater than the number given above, as may be seen by the following table :—

Co-efficients of expansion for 1° C.

Unliquefiable.

Air	·003665
Nitrogen	·003668
Hydrogen	·003667
Carbonic oxide	·003667

Liquefiable.

Carbonic anhydride	·003688
Nitrous oxide	·003676
Cyanogen	·003829
Sulphurous anhydride	·003845

It seems not unreasonable to suppose that such differences are due in part to the fact that in vapours and in the liquefiable gases the influence of cohesion is not altogether annulled. It is conceivable that a vapour may consist of molecules which, unlike the independent and mutually repulsive molecules of perfect gases, may be connected together into companies, which move about much in the same way as individual molecules, but less rapidly.

Examples.—A certain mass of air measures 100 cubic centimetres at 0°; to find its volume at 10°.

273 vols. of a gas at 0° become 273 + t vols. when the temp. is t° C.

In this case t = 10,

Then 273 c.c. at 0° become 283 c.c. at 10°.

1 c.c. „ „ becomes $\frac{283}{273}$ c.c. at 10°.

And 100 c.c. „ „ „ $\frac{283 \times 100}{273}$ c.c. at 10°.

Ans. 103·66 c.c.

Or employing the decimal equivalent to $\frac{1}{273}$, let V_1 be the required volume and V the vol. given.

$$\text{Then } V_1 = V (1 + \cdot 00366 \, t)$$
$$= 100 (1 + \cdot 00366 \times 10)$$
$$= 103 \cdot 66 \text{ Ans.}$$

300 c.c. of air at 20°; find the volume at 0°.

273 + 20 at 20° become 273 at 0°

    1   ,,   becomes $\dfrac{273}{293}$ at 0°

And 300   ,,   ,, $\dfrac{273 \times 300}{293}$ at 0°

279·5 Ans.

Or, using the decimal co-efficient, we say V_0, a certain volume of air at 0°, becomes 300 c.c. at 20°, or

$$V_0 (1 + \cdot 00366 \times 20) = 300$$

Whence $V_0 = \dfrac{300}{1 + \cdot 00366 \times 20} = 279 \cdot 5$ c. c. Ans.

500 c.c. of air at 10°; find the volume at − 10°.

In this and all similar problems it is to be remembered that the co-efficient of expansion is a fraction of the volume which the gas occupies at 0°, not at any other temperature.

273 + 10 c.c. of air at 10°

measure

273 − 10 c.c. at − 10°

Therefore 500 c.c. of air at 10°

measure $\dfrac{263 \times 500}{283}$ or 464·6 c.c. at − 10°

Or let V_{10}, V_0, and $V-_{10}$, be the volumes at the temperatures 10°, 0°, and − 10° respectively; then

$$V-_{10} = V_0 (1 - \cdot 00366 \times 10) = \dfrac{V_{10}}{1 + \cdot 00366 \times 10} \times (1 - \cdot 00366 \times 10)$$
$$= 464 \cdot 6 \text{ c.c.   Ans.}$$

Air or any other permanent gas diminishes by $\frac{1}{273}$ of its volume for every degree of temperature travelling down the scale. If the same relations of volume to temperature

were maintained, it is obvious that at $-273°$ the volume would be *nil*, and the gas cease to exist. Such a temperature has, however, never been attained ; and if ever such a degree of cold were reached, there can be no doubt that a gas exposed to it would liquefy, or that some change would occur whereby the gas would be released from obedience to the ordinary law.

Notwithstanding, however, that such a condition of things is practically beyond the reach of experiment, this consideration is important as furnishing the basis of an absolute scale of temperature. Calling $-273°$ C the zero point, we represent absolute temperatures by adding 273 to the number of degrees upon the ordinary Centigrade scale. From what has already been stated regarding the expansion of gases, it follows that pressure being constant, the volume of a mass of gas varies directly as the absolute temperature. This statement is sometimes referred to as the law of Charles, to whom we owe the discovery* of the equal expansibility of the principal gases by heat.

LAW OF AVOGADRO.

It has been shown in the foregoing paragraphs that all gases, when under conditions sufficiently remote from those which induce their liquefaction, are affected in the same manner and to the same extent by changes of pressure and of temperature. Differences of density, of chemical composition, or of chemical properties, do not affect the generality of this statement. The volumes of heavy oxygen and light hydrogen, of simple nitrogen and compound marsh gas increase and decrease according to the same law. It is impossible to avoid the inference from these facts that these gases, so different chemically, must be physically constituted alike. If now we admit the hypothesis that gases, like other bodies, are made up of small independent

* Towards the end of the last century.

masses called molecules, and that heat causes these mole-
cules to separate from one another, whilst cold or pressure
causes them to approach, we are led to the assumption
that in equal volumes of different gases* there must exist
the same number of molecules.

This statement, originally enunciated by an Italian
physicist, Avogadro, in 1811, may now be regarded as a
well-established truth.

But, like every other part of the molecular theory, this
law owes its recognition by physicists and chemists not to
any direct proof that can be adduced from experimental
sources in support of such hypotheses, but to the fact that
nearly all observed chemical phenomena do not only
harmonise with such views, but find in them complete and
satisfactory explanation.

Admit the law of Avogadro, and we see at once why
gases are equally expanded by heat, why they are equally
contracted by cold and pressure, and why they combine
together, according to the discovery of Gay-Lussac, in
simple proportions by volume.

In a later chapter will be shown some of the consequences
which follow upon an application of this law, and the im-
portant progress of chemical theory which has resulted
from its adoption.

* Under the same circumstances of temperature and pressure.

CHAPTER VII.

SPECTRA.—EMISSION SPECTRA.

All bodies when heated to a sufficiently high temperature emit light ; those which are densest being, as a rule, the most intensely luminous.

When this light is examined by a prism the image formed by the refracted and dispersed rays appears in the form of a coloured band, which is called the *spectrum*. The apparatus employed for the purpose of observing the spectra of different kinds of light is called a *spectroscope*. The details of its construction are described in nearly all works on physics. Suffice it, therefore, to say that the light under examination is allowed to pass first through a fine slit in a metallic plate so arranged that the slit is parallel to the edges of the prism. The rays are then rendered parallel, by means of a pair of lenses placed in a tube which is fixed at the angle of minimum deviation with the first face of the prism. After passing through the prism the light is viewed through a telescope, which gives a magnified image of the spectrum.

The spectrum of the light emitted by solids, liquids, and very dense gases, is found to be a continuous one, that is to say, the simple colours, red, orange, yellow, green, blue, indigo and violet, which are its components, merge one into the other gradually, and are not separated by dark intervals. The spectra furnished by ordinary gases or vapours, when ignited, consist, on the contrary, of bright lines, which are so many images of the slit of the spectroscope refracted in different degrees so as to be separated from one another. In the spaces between these bright bands there is in general no light. In some cases, however, a continuous spectrum is more or less distinctly visible.

These differences are shown as far as possible without the aid of colour in the following diagrams. The first represents

the appearance which is presented by the spectrum of an ignited solid, such as lime, or of a flame such as that of a candle, which is supposed to contain either solid matters or very dense vapours. The second is the spectrum of heated hydrogen gas.
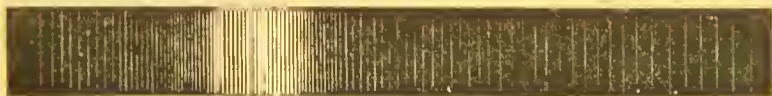
CONTINUOUS SPECTRUM.

BRIGHT LINE SPECTRUM.

Salts of the alkalis, of the alkaline earths, of copper and many other metals, have long been known to give light having peculiar and characteristic colours when heated in the blow-pipe flame or in the non-luminous flame of the Bunsen burner. Thus, sodium salts give yellow light, potassium violet, barium green, calcium orange-red, and lithium and strontium crimson flames.

When flames coloured by the vapours of these salts are viewed with the spectroscope, they are found to exhibit a character similar to that of the gas hydrogen. That is to say, these spectra are made up of bright lines which are separated from each other by dark intervals. The appearance shown in each case is indicated by the diagrams on next page.

When the same prism is employed these lines always occupy the same relative positions, and the lines produced by any one substance are not changed in position, or breadth, or intensity in the presence of another substance which, when ignited, gives out a different kind of light.

Thus, if a flame coloured by sodium or one of its salts is viewed through the spectroscope, the bright yellow double band characteristic of sodium is alone visible.

Another flame coloured by some compound of potassium gives only the red and deep blue lines peculiar to the ignited vapour of that metal. A third flame, into which is
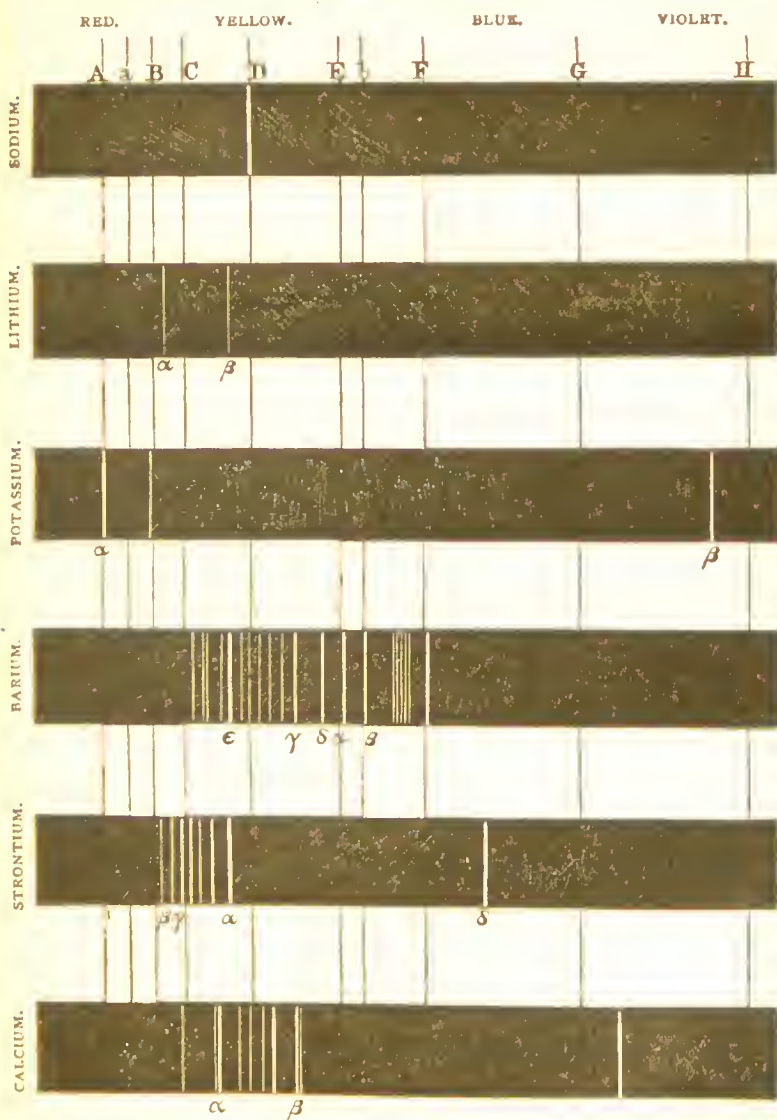
introduced a mixture of potassium and sodium salts, appears

yellow to the unaided eye, if the proportion of sodium present is more than infinitesimal. But after passing through the prism of the spectroscope this yellow light is resolved into red and indigo potassium bands and the yellow sodium lines occupying exactly the same position as when observed separately. These facts constitute the basis of the method of spectral analysis.

It is only necessary to bring before the slit of the spectroscope the incandescent vapour of a metal or other substance which it is desired to examine. The position and number of the bright lines visible through the telescope are at once an indication of the nature of the substance. The volatilisation of solid bodies and the necessary ignition of the vapour is effected most generally by the aid of the Bunsen gas-flame ; but when this is incompetent to produce a temperature sufficiently high, the oxy-hydrogen blow-pipe or the electric arc may be employed. The transmission of sparks from an induction coil between terminals to which metals can be attached is a convenient method for obtaining the spectra of such bodies as well as of gases such as nitrogen, hydrogen, and carbon dioxide, through which the sparks can be passed.

The delicacy of the method of spectral observation is very great, far surpassing that of the most exact and sensitive of chemical tests, and by its aid the presence of exceedingly minute quantities of various elements can be detected with certainty and ease. Sodium and lithium, for example, are bodies which, even in excessively small quantity, are capable of giving very easily recognisable spectra, and, accordingly, their presence has been discovered in many substances in which it was formerly unsuspected. Sodium salts are, indeed, almost universally diffused in water, in the mineral constituents of the soil, in the tissues of plants and animals, and even in the dust suspended in the atmosphere.

Spectroscopic analysis has also led to the discovery of

several elements previously unknown, and existing as unrecognised impurities in various substances. These newly-discovered elements are all metals. Their names are given below :—

NAME.	ORIGINAL SOURCE.	DISCOVERER.	DATE.
Rubidium	⎱ Dürckheim	Bunsen	1859
Cæsium	⎰ Mineral Water	,,	,,
Thallium	Seleniferous pyrites	Crookes	1857
Indium	Freiberg blende	Reich & Richter	1863
Gallium	Zinc blende	Lecoq de	1875
	from Pyrenese	Boisbaudran	

It will be seen by reference to the diagrams that the spectra of the metals of the alkalis and of the alkaline earths are comparatively simple, consisting, in most cases, of a small number of lines, which are often widely separated and easily recognised. Several other metallic elements, under the same conditions, yield equally simple spectra : that of thallium, for example, consisting of a single green line, whilst the spectrum of indium exhibits one line in the blue and another in the indigo. The spectra of the heavy and less volatile metals are, however, in general, much more complex ; the spectrum of iron, for instance, showing upwards of four hundred and fifty lines, many of them crowded together in the green.

When a compound, such as the chloride of a metal like sodium, is heated in the Bunsen flame, it gives out light which is very generally identical with the light obtained from the incandescent vapour of the metal itself. Sometimes, however, this is not found to be the case, and the spectra of certain compounds is different from that of either of the constituents, taken separately, and is, in general, more complex.

The accompanying diagram exhibits a comparison of the spectra obtained by the introduction of solid calcium chloride into the non-luminous gas flame, and when the electric spark is passed over the same compound.

The higher temperature in the second case causes a decomposition of the compound, and the observed lines, which are changed both in number and in refrangibility, are attributed to the glowing vapour of the metal calcium itself.

The position of such lines is not altered at still higher temperatures, though not unfrequently new lines make their appearance.

ABSORPTION SPECTRA.

When a transparent coloured medium, such as a piece of glass or a coloured liquid, is brought into the path of a ray of light before it enters the spectroscope, certain portions of the spectrum disappear. The bands of darkness which are thus produced are due to the interception of certain portions of the light by the coloured glass or solution, or vapour, as the case may be. The resulting spectrum is called an *absorption spectrum*. It presents characteristics which in many cases are as decided as those of the emission spectrum, and the observation of absorption spectra may occasionally be turned to practical account in the recognition of the colouring matter of blood, of wines, and many other substances, as well as of certain coloured gases and vapours.

When the absorbing medium is the vapour of an element

or of a compound which is volatile without decomposition, the dark lines of absorption occupy the same position as the bright lines in the spectrum of the light produced by the ignition of the same vapour. Thus, if a beam of light from a lamp is allowed to traverse a sufficiently thick stratum of sodium vapour, two dark lines close together make their appearance in the yellow ; and if such a spectrum is viewed side by side with the ordinary spectrum of the monochromatic sodium light, the position of the dark absorption band is seen to coincide with that of the bright yellow lines. Such phenomena are explained by the law that gases and vapours are capable of absorbing and stopping the same rays of light which they emit at higher temperatures, when in the state of ignition or incandescence.

This law has been experimentally verified by the examination not only of the absorption spectrum of sodium, but of other elements which give more complex spectra. The facts thus established have been employed in the solution of the very interesting problem presented by the light which reaches us from the sun and other heavenly bodies. Sunlight examined by a spectroscope exhibits a spectrum from which none of the primary colours are absent, but which is traversed by a very large number of fine black lines, many of which were discovered so long ago as 1814 by a German optician, Fraunhofer. They are usually known as Fraunhofer's lines.

In the figure, the position of a few only of the most prominent is indicated, and they are distinguished by the letters used originally by Fraunhofer.
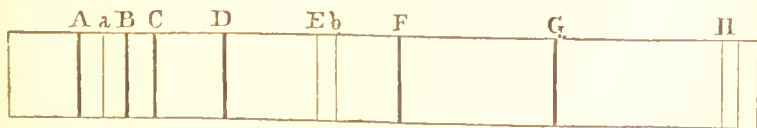
These dark spaces are now known to be absorption bands. It has been found that their positions coincide with

the lines of the spectra of many terrestrial elements ; and the coincidences which have been observed are so absolute and so numerous as to lead to the inevitable conclusion that they are produced by the vapours of such bodies existing in the gaseous envelope of the sun.

It is beyond the purpose of this book to give further details with regard to this most interesting question, which is, moreover, fully treated of in several well-known works specially devoted to the subject.

THERMAL AND CHEMICAL SPECTRA.

The eye enables us to recognise only a part of the spectrum of a luminous object. In addition to the rays which give the impression of light, there are others which produce heating effects, and others, again, the special function of which is to promote chemical combinations and decompositions.

A sensitive thermometer exposed successively to different portions of the visible spectrum will indicate that the heating effect is produced only towards the red end, and even that the maximum is attained amongst rays which are less refrangible than the extreme end of the visible red, and the spectrum of which lies beyond in darkness. The yellow and red luminous rays and the dark heating rays possess, however, little or no chemical power. This accords with the experience of photographers, who are accustomed to manipulate their sensitive plates in rooms illuminated by yellow light. The chemically active rays are confined almost entirely to the violet end of the spectrum, the exact position of the most active being found, however, to depend to a certain extent upon the nature of the substance submitted to their influence. Thus, silver salts are blackened, and hydrogen and chlorine are caused to combine most rapidly when exposed to that part of the violet end situated between the lines G and H of the solar spectrum, though more or less chemical activity is manifested some distance

beyond the visible violet on the one side and as far as the middle of the green on the other; all perceptible action ceasing in the yellow or most luminous position of the visible spectrum.

These relations are exhibited by the three curves in the following diagram :—
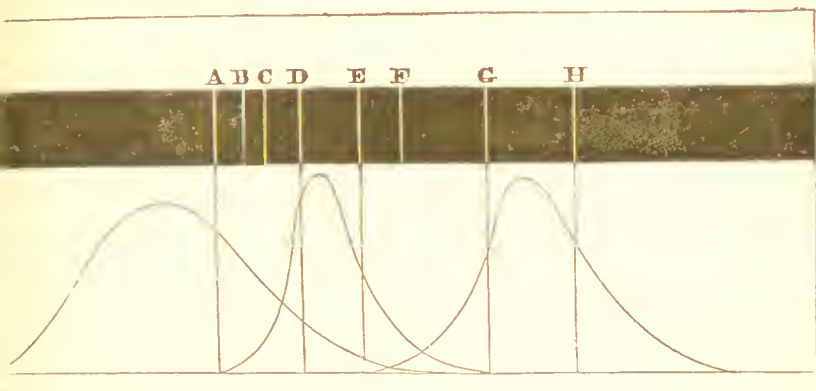
The summit of each curve indicates the position of the maxima of heating, luminous, and chemical effects in the spectrum of sunlight, the vertical lines representing the chief dark lines in the solar spectrum.

These curves are represented as overlapping one another, but it must not be supposed from this that there are three distinct sets of rays in the spectrum. In all probability the rays are of the same kind from end to end, but differ in wave-length and rapidity of vibration. The least refrangible rays are capable of producing the effects of heat, but are not capable of exciting the sensations of vision, whilst the vibrations which communicate the sensation of violet to the eye are also capable of effecting chemical change.

LUMINOSITY OF FLAME.

The cause of the luminosity of common candle and gas flames has long been a subject of interest, and two chief hypotheses have been framed with the object of explaining

it. Though neither of these hypotheses alone is capable of furnishing a complete explanation of every case, yet, taken together, they serve to account satisfactorily for the phenomena which are usually observed.

According to the earlier hypothesis, proposed in 1817 by Sir H. Davy, the luminosity of flame is attributed to the existence in the flame of particles of solid matter, which, being heated to a high temperature by the burning gases, emit light. These solid matters, supposed to exist in the flame, are deposited in the form of soot when a cold body is plunged into the flame. Such facts as the following were adduced by Davy in support of this hypothesis.

The flame of hydrogen or of alcohol, burning in the usual way, emits only a very feeble light; but the introduction of solid matter, such as powdered charcoal, oxide of zinc, or dust of any kind, whether combustible or not, serves to render such a flame luminous.

A bright flame is also produced by the combustion, in air or oxygen, of substances which, like metallic zinc, form solid products of combustion. On the other hand, sulphur, hydrogen, and carbonic oxide, which, in burning, yield entirely gaseous products, give out light very sparingly.

The spectroscope has also shown us that ordinary luminous flames yield a continuous spectrum of the same character as that usually produced by incandescent solids.

The production of solid particles in a candle flame, or in the flame of coal-gas, or other hydrocarbon, is supposed to be due to the selective power of the oxygen of the air, in virtue of which it unites preferably with the hydrogen, leaving a part of the carbon in a solid form to be consumed as it reaches the higher parts of the flame.

A candle flame burning steadily exhibits the form of a long cone with the apex pointing upwards. Other flames taper upwards in the same way. This form is, of course, due to the strong upward current produced in the air which immediately surrounds the flame, in consequence of the

heat. A close examination of the flame of a candle will show that it consists of several parts. At the base is a faintly luminous stratum of a blue colour. Higher up the luminosity increases, the most intense light proceeding from those parts which are near the middle ; whilst the whole structure is surrounded by a transparent and almost invisible, but very hot, envelope of ignited gas. It is easy to show by many simple experiments that such a flame is only a shell of ignited gas, the process of combustion occurring only on the outside, the interior being filled with comparatively cool gas or vapour. Thus, if a sheet of paper is held for a moment horizontally across the flame it will receive a deposit of soot in the form of a ring. A slip of wood or a wire passed through the flame becomes ignited only at the two points where it cuts the outer portions of the flame, the part in contact with the interior remaining dark.

The luminosity of such a flame is diminished if a sufficient quantity of air or oxygen is thrown into it, and at the same time it loses the power of depositing soot upon any cold object held in it. The flames of the blowpipe and the Bunsen burner are produced in this way, and present this character.

Some experiments made a few years ago by Dr. Frankland, indicate that the ignition of solid particles of sooty matters in hydrocarbon flames may occasionally be the cause of the light emitted by such flames, but that in some cases at least the effect is not wholly attributable to this circumstance. Dr. Frankland has observed that when hydrogen is burnt in oxygen under great pressure the light of the flame, usually so pale, is increased to such an extent as to be capable of illuminating a page of print so that it can be read at some distance.

The spectrum of hydrogen burning under pressure exhibits the three bands characteristic of hydrogen, but much broader and more or less nebulous at the edges, so that an approach to a continuous spectrum similar to that

E

obtained from solid bodies is the result. A similar effect is produced by burning carbonic oxide. So that the argument founded upon the nature of the spectrum of an ordinary luminous flame has less weight than might otherwise be supposed.

Moreover, in burning a series of substances, all of which yield volatile products of combustion, it is found that many of them are capable of emitting a very vivid light, quite equal in brilliancy to the light produced by the ignition of many substances which are solid and not capable of vaporisation. Thus, the combustion of arsenic in oxygen is attended by the emission of a very brilliant white light, although all the substances present—the arsenic, the oxygen, and the arsenious oxide which is formed—are, at the temperature of ignition, entirely in a state of vapour.

In such cases, therefore, the light cannot be attributed to glowing solid matter. It has been observed that the brilliancy of the light emitted by the combustion of such substances is nearly proportional to the density of the ignited vapours existing in the flame, provided that in each case the temperature is sufficiently high.

In all probability, then, the luminosity of burning gas or tallow is due to the ignition of vaporous, but very dense, hydrocarbons, and is not to be ascribed to the presence of solid particles of carbon. The fact that ordinary flames are transparent is also difficult to reconcile with the latter hypothesis.

EXERCISES ON SECTION I.

1. Water is shaken up with a large volume of oxygen gas under a constant pressure of 765 mm. What volume of the gas will be contained in 10 c. c. of the solution?

2. Water is exposed to an atmosphere consisting of 21 vols. of oxygen, with 79 volumes of nitrogen.

Temp. $0°$; pressure, 760 mm.
Coeffs. of sol., $N = ·02$, $O = ·04$.

Calculate (*a*) the total volume of gas dissolved by 52·5 c. c. of water, and (*b*) the percentage composition of the gas.

3. Soda-water is charged under a pressure of 2·3 atmospheres. Calculate the volume of carbonic anhydride contained in 300 cubic-centimetres of such water.

> An atmosphere = 760 mm. barom.
> Coeff. of sol. for carbonic anhydride 1·7967.

4. Sulphur dioxide is passed into water as long as it is absorbed. If the barometer stands at 745 mm., calculate the volume of gas contained in half a litre of the solution.

> Coeff. for sulphur dioxide, 79·789.

5. Water is shaken up with its own bulk of a mixture of 1 volume of oxygen with 3 vols. of nitrogen. Supposing the temp. and pressure to remain normal and constant throughout the experiment, calculate the composition of the residual air.

> Coeff. of oxygen, ·04114
> Coeff. of nitrogen, ·02035

Diffusion of Gases.

6. The specific gravity of chlorine is 35·5 (H = 1). Compare its velocity of diffusion with that of hydrogen.

7. Specific gravity of ozone, 24; of carbonic anhydride, 22. Compare their velocities of diffusion with each other and with that of H (sp. gr. 1).

8. The rate of diffusion of a gas is observed to be ·81 when that of air is 1. Find its density.

9. Oxygen and hydrogen are separated by a porous plate, and 3·83 cubic-centimetres of hydrogen pass through the plate in a second, what volume of oxygen passes during the same time in the opposite direction?

10. In the last question, suppose the original volume of the oxygen to have been 20 c. c., what will be the composition of the mixture formed in its place after three seconds, assuming the apparatus so arranged that no change of pressure occurs?

Corrections of Gas-volumes for Changes of Pressure and Temperature.

11. 100 c. c. of air when bar. = 750 mm. Find the volume when bar. = 790 mm.

12. 250 c. c. of air when bar. = 765 mm. Find the volume when bar. = 745 mm.

13. What pressure in atmospheres would be required to make the density of hydrogen (sp. gr. ·0693) equal to that of air?

14.   Calculate the atmospheric pressure per square centimetre when the barometer stands at 760 mm.

Weight of 1 c. c. of mercury 13·596 grams.

15. Find the atmospheric pressure per square decimetre when the barometer stands at 750 mm.

16. What change of atmospheric pressure will be denoted by a change of 12 mm. in the barometric column.

17. The weight of one litre of hydrogen at 0° and 760 mm. is ·0896 gram or 1 crith.   Calculate the weight of 1 litre of hydrogen measured off under a pressure of 1400 mm.

18. Find the weight of 1 litre of nitrogen (sp. gr. 14) ; of 10 litres of carbonic anhydride (sp. gr. 22) ; of 250 c. c. of oxygen (sp. gr. 16).

19. A mass of air at 0° measures 100° c. c. What volume will it occupy at 20° ; at 15°·5 ; at 100° ?

20. A certain quantity of air is measured at 75°.   What volume will it have at 0° ?

21.   1000 c. c. of a gas at 12°·5.   What volume at 75°?

22.   500 c. c. of a gas at 10°.   What volume at 40°?

23.   300 c. c. of a gas at 25°.   What will its volume be at − 10° ?

24.   75 c. c. of nitrogen measured at 50°.   What volume at − 35° ?

25.   1500 c. c. of hydrogen measured at 20°.   At what temperature will it measure 1000 c. c. ?

26.   Five degrees centigrade correspond with nine degrees on the Fahrenheit scale.   Find the co-efficient of expansion of gases for 1° F.

27.   150 c. c. of nitrogen are measured at 10°, and under a pressure of 500 mm. of mercury.   What will the volume become at 16°·4 when the pressure is 540 mm.?

28.   A quantity of nitrogen confined in a tube standing over mercury in a mercurial trough measures 75·5 c. c. ; temp. 15° ; bar. 742 mm. ; surface of mercury inside the tube above surface of mercury in the trough 122 mm.   Find the volume which the gas would occupy at normal temperature and pressure.

29.   1000 cubic feet of gas are put into a balloon of 1250 cubic feet capacity ; temp. 18° ; bar. 765 mm.   After ascending a certain height it is found to be fully distended. What is the atmospheric pressure, temperature being 8° ?

30.   A certain balloon is just capable of holding 10 grams of hydrogen under standard conditions : what is its capacity ?   How much larger must it be made if it is required to sustain a diminished atmospheric pressure equal to 650 mm. bar. ?

SECTION II.

CHAPTER VIII.

ELEMENTS AND COMPOUNDS.

WHEN water is exposed to a very high temperature or made the vehicle of an electric current, it disappears and is replaced by an equal weight of a mixture of two gases, hydrogen and oxygen. These two gases will, under certain conditions, again give rise to water and to exactly the same amount of water as at first.

Water then is said to be composed of oxygen and hydrogen. It is worth noting, however, that strictly speaking this can only mean that in proportion as the water is destroyed or ceases to exist, the gases make their appearance, and *vice versa*, for in water we have no resemblance to hydrogen or oxygen, neither can we detect either of those bodies in water except by this process of so-called *decomposition.**

Now, if the hydrogen thus obtained from water is submitted to a repetition of the same kind of treatment or to any other that may suggest itself, it refuses utterly to yield up anything that is not hydrogen. In other words, it cannot

* "Cavendish and Watt both discovered the composition of water. Cavendish established the facts; Watt, the idea. Cavendish says, 'From inflammable air and dephlogisticated air water is produced.' Watt says, 'Water consists or is composed of inflammable air and dephlogisticated air.' Between these forms of expression there is a wide distinction."—*Liebig's Letters on Chemistry*, p. 58.

be decomposed. We find then that certain bodies,* such as water, may be resolved into two or more different kinds of matter, and these are called *compounds* ; whilst others like hydrogen cannot be split up in this manner by any means with which we are at present acquainted, and are regarded as *elements*.

Instances, however, have not been wanting of bodies for a long time regarded as chemical elements ultimately showing their true character as compounds under the influence of some new agent or some improved mode of operating. For example, the alkalies potash and soda were regarded as elementary till Sir H. Davy showed them to be compounds of the metals potassium and sodium with oxygen and hydrogen, and the body represented as metallic vanadium by Berzelius turned out to be an oxide of vanadium when examined long afterwards by Roscoe. This term element is, therefore, used in no absolute sense, but is merely intended to imply that in the present state of knowledge the bodies thus designated must be regarded as simple substances.

In the case of oxygen it is found that, by the action of electricity and otherwise, it may be converted into another gas, ozone, possessing remarkable characters quite distinct from those of oxygen. Nevertheless, oxygen ranks as an element because it yields in this way only one new body at a time, which by mere application of heat recovers its original properties, and that without loss or gain in weight. It must, therefore, be assumed that the altered properties exhibited under these circumstances are owing to a temporary re- arrangement of its constituent particles. When, as in this case, elementary matter, stuff, or substance is capable of making its appearance in the form of two or more bodies having different properties, these are said to be *allotropic* modifications of the element, and the phenomenon is spoken of as allotropy. (See Isomerism, Chap. XX.)

* It must be understood that bodies of definite characters, and not mere mixtures, are here referred to. (See Chap. XI.)

About sixty-three elements are known at the present time, but it is not improbable that a few new substances may be hereafter added to this number. It is not, however, very likely that any hitherto unknown elements will be found to occur in any considerable quantity among the constituents of the earth's crust, for every substance within reach of man has already been subjected to a very close scrutiny by chemists.

It will be seen by reference to the following table that the materials which compose the solid earth, so far as we know it—the ocean, the atmosphere, and the bodies of the living beings which inhabit it—are made up of a few of these elements, the rest occurring in much smaller quantity, in some cases discoverable only by specially delicate methods :

Water consists of . . . . { Hydrogen. / Oxygen.

Air consists chiefly of . . . . . { Oxygen. / Nitrogen.

Solid Earth consists chiefly of

Silica . . . = { Silicon. / Oxygen.

Limestone . . = { Calcium. / Magnesium. / Carbon. / Oxygen.

Various silicates forming crystalline rocks or beds of clay. { Silicon. / Oxygen. / Aluminium. / Iron. / Calcium. / Potassium.

Plants consist chiefly of . . . . . { Carbon. / Hydrogen. / Oxygen.

Animals consist chiefly of . . . { Carbon. / Hydrogen. / Oxygen. / Nitrogen.

Chemists have found it convenient to adopt a system of symbols and formulæ, whereby to represent the elements and those compounds the composition of which is known.

Thus, to each of the elements is assigned a symbol formed generally of the initial letter of the Latin name of the element. For example, sulphur is represented by the symbol S; selenion, Se; silicon, Si; strontium, Sr; but silver (*argentum*) is Ag, and sodium (*natron*) has the symbol, Na.

But chemical symbols are not merely abbreviations contrived, like shorthand characters, for the purpose of saving trouble in writing the names. Each symbol represents *one atom* of the element for which it stands, and hence expresses a definite weight and volume of the element, which are identical with the proportions by weight and volume in which it enters into chemical combination.

The weight of an atom of hydrogen is less than the weight of an atom of any other element. It is, therefore, convenient to consider the value of the symbol of hydrogen as unity and the values of all other symbols greater than unity. But since nothing is known as to the absolute weight of an atom of hydrogen or of any other element, it should be borne in mind that the atomic weights are in reality ratios or fractions, whose denominator is 1, although they are always written in the form of whole numbers.

In the following list are given the names of all the known elements, together with their symbols and atomic weights, and the student is recommended at once to commit to memory those which are printed in capital letters, leaving the rest to be learnt gradually as occasion may require :—

	Name of Element.		Symbol.			Atomic Weight.
1	ALUMINIUM	.	Al	.	.	27·3
2	Antimony	.	Sb (Stibium)		.	122
3	Arsenic .	.	As	.	.	75
4	Barium .	.	Ba	.	.	137
5	Bismuth .	.	Bi	.	.	210
6	Boron .	.	B	.	.	11
7	BROMINE .		Br	.	.	80
8	Cadmium	.	Cd	.	.	112
9	Cœsium .	.	Cs	.	.	133
10	CALCIUM .	.	Ca	.	.	40
11	CARBON .	.	C	.	.	12
12	Cerium .	.	Ce	.	.	92
13	CHLORINE .	.	Cl	.	.	35·5
14	Chromium	.	Cr	.	.	52
15	Cobalt .	.	Co	.	.	58·7
16	COPPER .	.	Cu (Cuprum)	.		63·5
17	Didymium	.	D	.	.	95
18	Erbium .	.	E	.	.	113
19	FLUORINE .	.	F	.	.	19
20	Glucinum	.	Gl	.	.	9·3
21	Gold .	.	Au (Aurum).		.	197
22	HYDROGEN	.	H	.	.	1
23	Indium .	.	In	.	.	113·4
24	IODINE .	.	I	.	.	127
25	Iridium .	.	Ir	.	.	197
26	IRON .	.	Fe	.	.	56
27	Lanthanum	.	La	.	.	93
28	LEAD .	.	Pb (Plumbum)		.	207
29	Lithium .	.	Li	.	.	7
30	MAGNESIUM	.	Mg	.	.	24
31	Manganese	.	Mn	.	.	55
32	MERCURY .	.	Hg (Hydrargyrum)			200
33	Molybdenum .	.	Mo	.	.	96
34	Nickel .	.	Ni	.	.	58·7
35	Niobium	.	Nb	.	.	94
36	NITROGEN .	.	N	.	.	14
37	Osmium .	.	Os	.	.	199
38	OXYGEN	.	O	.	.	16
39	Palladium	.	Pd	.	.	106·5
40	PHOSPHORUS	.	P	.	.	31
41	Platinum	.	Pt	.	.	197·5
42	POTASSIUM	.	K (Kalium) .		.	39·1
43	Rhodium	.	Ro	.	.	104·5
44	Rubidium	.	Rb	.	.	85·4
45	Ruthenium	.	Ru	.	.	104·5
46	Selenion	.	Se	.	.	79 5

	Name of Element.			Symbol.			Atomic Weight.
47	SILVER	.	.	Ag (Argentum)		.	108
48	SILICON	.	.	Si	.	.	28
49	SODIUM	.	.	Na (Natrium)		.	23
50	Strontium	.	.	Sr	.	.	.	87·5
51	SULPHUR	.	.	S	.	.	.	32
52	Tantalum	.	.	Ta	.	.	.	182
53	Tellurium	.	.	Te	.	.	.	128
54	Thallium	.	.	Tl	.	.	.	203·5
55	Thorium	.	.	Th	.	.	.	116
56	Tin	.	.	Sn (Stannum)		.	118
57	Titanium	.	.	Ti	.	.	.	50
58	Tungsten	.	.	W (Wolfram)		.	184
59	Uranium	.	.	U	.	.	.	240
60	Vanadium	.	.	V	.	.	.	51
61	Yttrium .	.	.	Y	.	.	.	61·7
62	ZINC .	.	.	Zn	.	.	.	65
63	Zirconium	.	.	Zr	.	.	.	89·6

In order to indicate combination between two elements their symbols are placed side by side, thus, HCl. When a molecule of a compound contains more than one atom of each or either of its constituents, the number of atoms is indicated by a small figure placed below the line.

Thus the formula for water OH_2 represents one atom of oxygen united with two atoms of hydrogen, and H_3PO_4 means that three atoms of hydrogen, one atom of phosphorus, and four atoms of oxygen are bound together in phosphoric acid.

The formula, taken as a whole, is invariably assumed to represent *a molecule* of the compound, and the relative weight of this molecule is easily found by adding together the weights represented by the several symbols of which it is made up. This weight is called the molecular weight. In order to express two or more molecules a figure is placed at the beginning of the formula, and must be understood to multiply every symbol that follows it. For example, $2OH_2$ represents two molecules of water, each consisting of two atoms of hydrogen with one atom of oxygen; in all, four atoms

of hydrogen and two atoms of oxygen. Occasionally brackets have to be introduced when some group of symbols occurs more than once. Aluminium sulphate, for example, has the formula $Al_2(SO_4)_3$, which is thus written for the sake of assimilating the appearance of the formula to that of other sulphates, such as H_2SO_4, $BaSO_4$, $FeSO_4$ &c. Resemblance between them would be less apparent if it were expressed as $Al_2 S_3 O_{12}$.

Care and a little practice are all that is necessary to avoid confusion in the use of formulæ, and the student is therefore recommended to work out conscientiously all the examples given at the end of the section.

CHAPTER IX.

LAWS OF CHEMICAL COMBINATION.

The extraction of the metals from their ores, the manufacture of alkalies, soap, glass, dyes, and a variety of other useful applications of practical chemistry, were known to man in a more or less practical form from very early times. The alchemists extended the art of chemistry by the discovery of the processes for producing many acids and salts, and by the invention of much useful apparatus. The discovery of oxygen by Priestley, of chlorine by Scheele, the proof of the composition of water supplied by Cavendish, and the overthrow of the phlogistic theory by Lavoisier's explanation of combustion, were all great strides in advance which followed one another in rapid succession. But the foundation of chemistry as an exact science was only laid towards the end of the last century, when the balance began to be used systematically in all chemical investigations. Exact determinations of the relative weights of bodies engaged in various chemical reactions were necessary for the establishment of those laws upon which chemical ideas

of the present day are founded. If we start by admitting the molecular constitution of matter, it becomes unnecessary to make any formal statement of the laws which have been found to regulate the distribution of weight or quantity of matter involved in chemical actions. If we assume, for example, that the element oxygen is made up of molecules, all having the same properties and each composed of two atoms whose weight is sixteen times that of the hydrogen atom, it is obvious that only a definite number of those atoms can take part in forming a chemical compound. And if, as we believe, these atoms are indestructible by the chemical force, no fractional part of an atom can enter into such process ; and if the number of atoms thus employed be represented as n, the weight of the substance will be 16n.

But since the molecular theory was not always employed by chemists, and even at the present day is not adopted universally, it is desirable still to indicate the facts which have been observed in connection with this question. The three general statements or laws may be expressed as follows :—

LAW OF DEFINITE PROPORTIONS.

The proportions in which bodies unite together chemically are definite and constant. In other words, a given chemical compound always consists of the same elements united in the same proportions.

In order to form water, for example, union between hydrogen and oxygen occurs exactly in the proportion of two measures of the former to one measure of the latter. This corresponds with two parts by weight of hydrogen to sixteen parts by weight of oxygen, since oxygen is sixteen times heavier than hydrogen. The employment of any larger quantity of either element would only result in the excess being left uncombined.

LAW OF MULTIPLE PROPORTIONS.

When one body unites with another in several proportions, these quantities have a simple relation to one another. Oxygen combines with carbon, forming two oxides of carbon. In the one, three parts by weight of carbon are united to four parts of oxygen, whilst in the other three parts of carbon combine with twice this quantity or eight parts of oxygen. A great number of equally simple cases might be cited, and, doubtless, it was the study of such cases which in the first instance led to the enunciation of the law. In perhaps a still greater number of instances, however, it is by no means easy to trace its application. Among the numerous compounds of carbon with hydrogen, for example, are found such relations as the following, which represent the composition of the series of paraffins :—

				Carbon.		Hydrogen.	
Methane	.	.	.	3	parts with	1	part
Ethane	.	.	.	4	,,	1	,,
Propane	.	.	.	9	,,	2	,,
Butane	.	.	.	24	,,	5	,,
Pentane	.	.	.	5	,,	1	,,
Hexane	.	.	.	36	,,	7	,,
Heptane	.	.	.	21	,,	4	,,
Octane	.	.	.	16	,,	3	,,
Nonane	.	.	.	27	,,	5	,,
Decane	.	.	.	60	,,	11	,,
&c.				&c.		&c.	

LAW OF RECIPROCAL PROPORTIONS.

The weights of two different elements, A and B, which combine with a third, C, represent the proportions in which they will themselves unite together if union between them is possible, or they bear some simple relation to those proportions. Thus, $35\frac{1}{2}$ parts of chlorine and 80 parts of bromine combine with 23 parts of sodium. Then, according to the law, when chlorine combines with bromine,

$35\frac{1}{2}$ parts of the former are required for every 80 parts of the latter. This may be rendered graphically somewhat in this manner :—

Sodium.

m 23.

n 80

Bromine.   with   p 35·5
                                                              Chlorine.
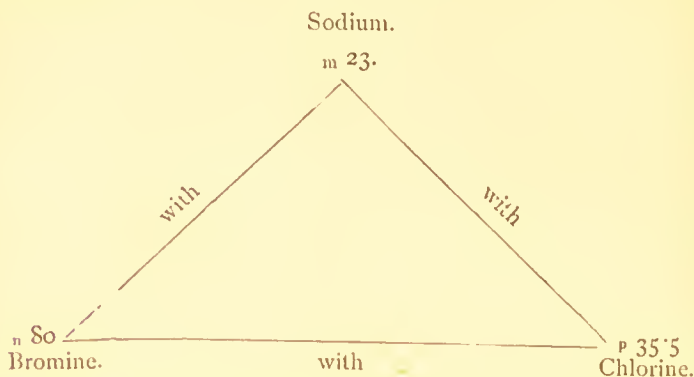
In other words, the combining weight of a body may always be represented as a multiple of the same number whatever state of combination it enters into, or $m\,n$ is the combining weight, where m is a number peculiar to the body and n is some integer.

LAW OF VOLUMES.

When gases combine together they do so in equal volumes, or in volumes which have some simple relation one to another, as 1 to 2, 1 to 3, 2 to 3, and so on. For example, hydrochloric acid is formed by the union of

    1 volume of hydrogen with
    1 volume of chlorine ;

water is formed by the union of

    2 volumes of hydrogen, with
    1 volume of oxygen ;

ammonia by the combination of

    3 volumes of hydrogen with
    1 volume of nitrogen ;

nitrous anhydride by the combination of

    2 volumes of nitrogen with
    3 volumes of oxygen, &c.

These facts are recorded in the formulæ

$$HCl \qquad H_2O \qquad H_3N \qquad N_2O_3$$

by which these compounds are commonly represented.

It is important also to remember that whatever the volume of the vaporous elements before combination, the bulk of the resulting compound, measured in the gaseous state under the same conditions of temperature and pressure, is always *two volumes*.

This will be again referred to in connection with the methods employed for the determination of molecular weights, and until those subjects have been discussed the student must be content to take upon trust all statements concerning molecular volumes, weights, and formulæ.

This law was first enunciated by Gay-Lussac very soon after the laws of reciprocal and multiple proportions by weight had been established by Dalton. We now see the connection between them and the dependence of the one upon the other, though this relation, from want of accurate knowledge, was not at first admitted by Dalton and other chemists. Originally a fact, depending upon experimental evidence only, this statement of Gay-Lussac's now stands in the more important position of a logical deduction from another law, the law of Avogadro (Chap. VI. p. 37).

The results of analysis before Dalton's time were represented by numbers which expressed the proportion of each constituent in 100 parts of the compound. For example, in 100 parts of red oxide of copper there are—

Copper	88·8
Oxygen	11·2
	100·0

In black oxide of copper :—

Copper	79·87
Oxygen	20·13
	100·00

In carbonic oxide :—

Carbon	.	.	.	.	42.85
Oxygen	.	.	.	.	57.14

100.00

In carbonic anhydride :—

Carbon	.	.	.	.	27.27
Oxygen	.	.	.	.	72.72

100.00

Dalton discovered reciprocal and multiple proportions by stripping from them the disguise in which this mode of representing composition enveloped them. For by taking the proportion of some one of the elements in a series of similar compounds as unity, and ascertaining by calculation the proportions which the others bear to it, it is easy to show that these proportions are simple multiples one of another.

In the case of the two oxides of carbon, the composition of which has just been stated, if we calculate the ratio of the oxygen to the carbon in both of them, we find the proportion in the second double that in the first. Thus, taking the carbon as unity—

Carbon.		Oxygen.		Carbon.		Oxygen.
42.85	:	57.14	::	1	:	1.33
and 27.27	:	72.72	::	1	:	2.66

Then plainly

1.33	:	2.66	::	1	:	2

In other words, the proportion of oxygen by weight in carbonic anhydride gas is double that contained in carbonic oxide. Obviously the same fact may be expressed in another way by taking the oxygen as unity instead of the carbon :—

Oxygen.		Carbon.		Oxygen.		Carbon.
57.14	:	42.85	::	1	:	.750
72.72	:	27.27	::	1	:	.375

Then—

      ·750   :   ·375   ::   2   :   1

Or, we may say that carbonic anhydride contains half as much carbon as carbonic oxide. Similarly it will be found that the ratios of the oxygen in the several oxides of nitrogen, of sulphur, and of many of the metals are as 1, 2, 3, &c., to 1, 2, 3, &c., of the other constituent.

Looking about for an explanation of these observations of his, it occurred to Dalton to resuscitate the ancient theory of the limited divisibility of matter. According to this view, matter is made up of definite small parts or particles called " atoms," because it was assumed that they could not be in any way cut or divided. This assumption of finite particles as an explanation of the phenomena of chemical combination thus became the basis of the modern theory of molecules. But Dalton's term "atom" was applied indiscriminately to the ultimate particles of compound as well as elementary bodies. The relative weights also assigned to these atoms were inferred from the results of the analysis of only a few compounds. Consequently the word " atom " in the Daltonian system may be interpreted sometimes " molecule," sometimes " atom," and in other cases it corresponds to the term " equivalent," as those words are now understood by chemists.

CHAPTER X.

EQUATIONS.

CLASSIFICATIONS OF REACTIONS.

Equations.—Chemical changes involve neither the destruction nor the creation of matter, but simply a redistribution of the materials of which the acting masses are composed.

In order, therefore, to represent symbolically the results of any given action it is only necessary to write down the formulæ of the bodies engaged, and then to transpose their symbols in such a manner as to build up the formulæ of the bodies which are produced. We thus arrive at equations in which the signs $+$ $-$ and $=$ are employed, so far as the weights of matter are concerned, in the same sense as in algebra.

The following examples will serve to show the manner in which chemical equations are to be read, as well as the mode of investigating the relative weight of the bodies which are formed or decomposed. The student should practise reading equations aloud, or writing them out at full length, according to these instructions :—

Equation given,

$$\sqrt{} \quad 2HgO \quad = \quad 2Hg \quad + \quad O_2.$$

This means that two molecules, or 432 parts, by weight, of mercuric oxide yield two molecules, or 400 parts, by weight, of metallic mercury, and one molecule, or 32 parts, by weight, of oxygen.

Young students, however, would do well to ensure precision by filling up such a scheme as the following :—

	$2\,Hg\,O$	$=$	$2\,Hg$	$+\quad O_2$
No. of moleeules	2	give	2	and 1
Name . .	Mercuric oxide		Mereury	Oxygen
Wt. of 1 mol. .	$200 + 16 = 216$		200	32
Whole weight .	used 432		obtained 400	32

When gases or vaporisable bodies occur in such an equation we can express the volume of each by recollecting that, according to the law of Avogadro, the volumes of gaseous molecules under like conditions are equal. We may also connect together the weight and volume of a gas by applying a rule which will be more fully explained in the next section, namely, that the specific gravity of a body in

the gaseous state* is the half of its molecular weight. The weight of a molecule of carbonic anhydride, for example, is 44 : its specific gravity is, therefore, 22, and the weight of a litre of the gas is 22 times as great as the weight of a litre of hydrogen measured at the same temperature and pressure. Now, the weight of a litre of hydrogen at 0°C, and under a pressure equal to 760 mm. of the baro- metric column is ·0896 gram or 1 crith. Hence, we may say that a litre of carbonic anhydride weighs 22 criths, or, if the weight is to be expressed in grams, it will be 22 × ·0896 grams.
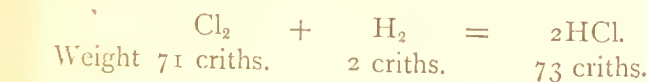
Example.
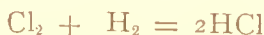
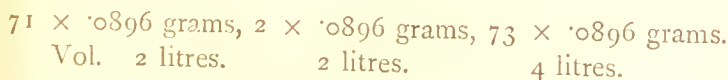$$Cl_2 + H_2 = 2HCl$$

A molecule of chlorine and a molecule of hydrogen pro- duce two molecules of hydrochloric acid.

	Cl_2	+	H_2	=	$2 HCl$
No. of Molecules	1		1		2
Name . . .	Chlorine		Hydrogen		Hydrochloric acid or hydrogen chloride.
Wt. of 1 molecule	71		2		36·5
Whole weight .	used 71		2		obtained 73
Volume . . .	,, 1		1		obtained 2
	or 2		or 2		or 4

If, now, we choose to attach a concrete value to the symbols, we express it thus :

$$Cl_2 + H_2 = 2HCl.$$
Weight 71 criths.   2 criths.   73 criths.
or

71 × ·0896 grams, 2 × ·0896 grams, 73 × ·0896 grams.
   Vol. 2 litres.   2 litres.   4 litres.

The student having thoroughly mastered the foregoing examples, and worked some of the exercises given at the end of the section, is now in a position to solve such pro-

* The specific gravity of hydrogen being taken as 1.

blems as the following, whieh may be taken as represen-
tative :—

1. How many pounds of zinc are required to make 500
pounds of the erystallised sulphate?

Formula of one moleeule of erystallised zinc sulphate,
$Zn\,SO_4\,.\,7H_2O$.

Molecular weight 287.

The symbol of zine, $Zn = 65$, oecurs only once in the
formula of the sulphate.   Hence,

In 287lbs. of zine sulphate there are   65lbs. of zine.

  1lb. ,, ,,   ,,   ,, ,, $\dfrac{65}{287}$lbs. of zinc.

∴ 500 lbs. ,, ,,   ,, would require $\dfrac{65}{287} \times$ 500lbs.

  Ans. $\dfrac{65 \times 500}{287} = \overset{\text{lbs.}}{113}\;\overset{\text{oz.}}{3\frac{5}{6}}$ of zinc.

2. How many litres of oxygen (at standard temperature
and pressure) are obtained by heating 10 grams of potassie
chlorate?

     $2KClO_3 = 2\,KCl + 3O_2$.
or more simply $KClO_3 =$ $KCl + 1\tfrac{1}{2}O_2$.
     126·6   74·6 48.
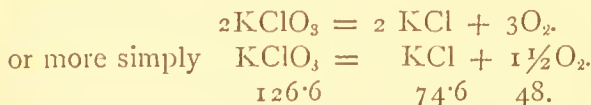
Taking the potassium chlorate in criths, we should obtain
3 litres of oxygen gas.   Then—

    122·6 criths

or   122·6 × ·0896 grams give 3 litres of oxygen.

   1 gram would give $\dfrac{3}{122\text{·}6 \times \text{·}0896}$ litres.

 ∴ 10 grams ,,   ,, $\dfrac{30}{122\text{·}6 \times \text{·}0896}$ litres.

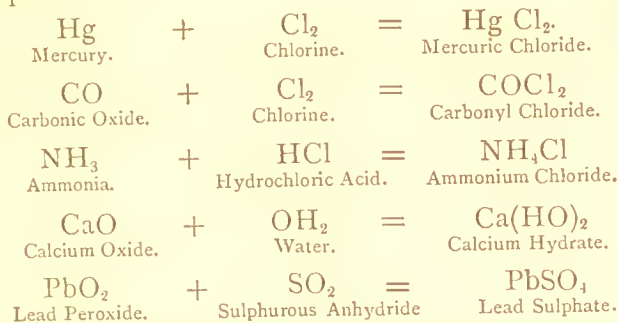 Ans. $\dfrac{30}{122\text{·}6 \times \text{·}0896} = 2\text{·}731$ litres, or 2731 c.e.

NOTE.—Taking ·0896 gram as the weight of 1 litre of hydrogen, 1 gram
is the weight of 11·16 litres. This numbei is sometimes useful.   Thus

CLASSIFICATION OF REACTIONS.

Chemical action may take place in a great many different ways, but every known chemical change to which bodies are subject may be referred to one or other of the following five typical modes of action :—
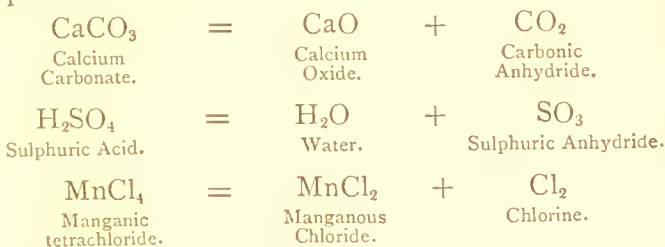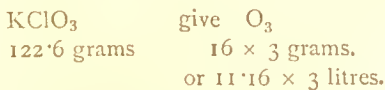
I.—*Combination of entire molecules.*

Examples—

$$Hg \quad + \quad Cl_2 \quad = \quad Hg\ Cl_2.$$
Mercury.   Chlorine.   Mercuric Chloride.

$$CO \quad + \quad Cl_2 \quad = \quad COCl_2$$
Carbonic Oxide.   Chlorine.   Carbonyl Chloride.

$$NH_3 \quad + \quad HCl \quad = \quad NH_4Cl$$
Ammonia.   Hydrochloric Acid.   Ammonium Chloride.

$$CaO \quad + \quad OH_2 \quad = \quad Ca(HO)_2$$
Calcium Oxide.   Water.   Calcium Hydrate.

$$PbO_2 \quad + \quad SO_2 \quad = \quad PbSO_4$$
Lead Peroxide.   Sulphurous Anhydride   Lead Sulphate.

II.—*Splitting up of a compound molecule into its elements, or into simpler molecules.*

Examples—

$$CaCO_3 \quad = \quad CaO \quad + \quad CO_2$$
Calcium Carbonate.   Calcium Oxide.   Carbonic Anhydride.

$$H_2SO_4 \quad = \quad H_2O \quad + \quad SO_3$$
Sulphuric Acid.   Water.   Sulphuric Anhydride.

$$MnCl_4 \quad = \quad MnCl_2 \quad + \quad Cl_2$$
Manganic tetrachloride.   Manganous Chloride.   Chlorine.

in the example worked out in the text, the calculation would be a trifle shorter, thus :

$$KClO_3 \qquad give \quad O_3$$
$$122 \cdot 6 \text{ grams} \qquad 16 \times 3 \text{ grams.}$$
$$\text{or } 11 \cdot 16 \times 3 \text{ litres.}$$

Then 10 grams of chlorate would give

$$\frac{33 \cdot 48 \times 10}{122 \cdot 6} \quad = \quad 2 \cdot 73 \text{ litres.}$$

$$Hg_2I_2 \quad = \quad Hg \quad + \quad HgI_2$$
Mercurous Iodide.   Mercury.   Mercuric Iodide.

$$C_7H_6O_5 \quad = \quad C_6H_6O_3 \quad + \quad CO_2$$
Gallic Acid.   Pyrogallol.   Carbonic Anhydride.
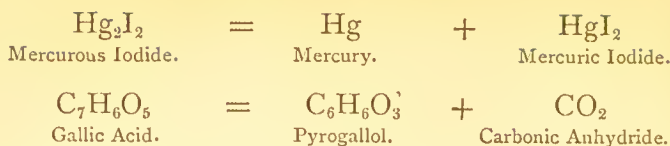
Many familiar decompositions, which at first sight appear to belong to this class, are in reality double decompositions, as an examination of one or two cases will show. The decomposition of mercuric oxide by heat, for example, seems to consist in a simple resolution of the body in its elements,

$$HgO \quad = \quad Hg \quad + \quad O.$$

But when we write the equation molecularly,

$$HgO \quad + \quad HgO \quad = \quad Hg \quad + \quad Hg \quad + \quad O_2,$$
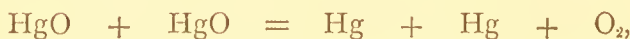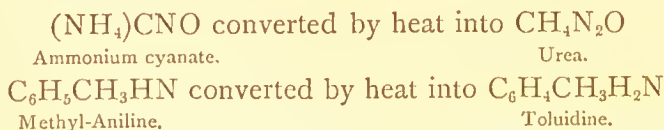
we may see that the decomposition of one molecule of the oxide necessitates the splitting up of another. In order to form one molecule of oxygen—and we believe one molecule to be the smallest quantity of the element capable of independent existence—we must take two atoms of it from two separate molecules of the oxide.

The same remarks apply to other cases, such as the decomposition of potassium chlorate by heat.

III.—*Rearrangement of the atoms constituting a molecule so as to give rise to a new body.*
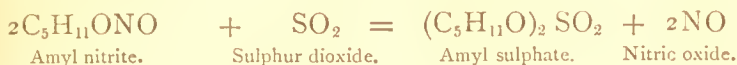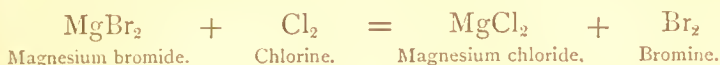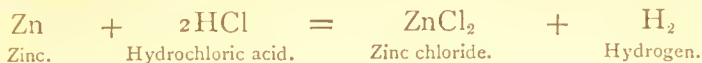
Two examples of this mode of transformation may be given here.

$(NH_4)CNO$ converted by heat into CH_4N_2O
Ammonium cyanate.   Urea.
$C_6H_5CH_3HN$ converted by heat into $C_6H_4CH_3H_2N$
Methyl-Aniline.   Toluidine.

The further explanation of this kind of change is postponed to the chapter on " Isomerism." (Sec. III.).

IV. *Single Metathesis.*—In this kind of change an atom, or group of atoms, contained in a molecule is displaced by another atom or group.

Examples.

$$Zn \quad + \quad 2HCl \quad = \quad ZnCl_2 \quad + \quad H_2$$
Zinc.   Hydrochloric acid.   Zinc chloride.   Hydrogen.

$$MgBr_2 \quad + \quad Cl_2 \quad = \quad MgCl_2 \quad + \quad Br_2$$
Magnesium bromide.   Chlorine.   Magnesium chloride.   Bromine.

$$2C_5H_{11}ONO \quad + \quad SO_2 \quad = \quad (C_5H_{11}O)_2 SO_2 \quad + \quad 2NO$$
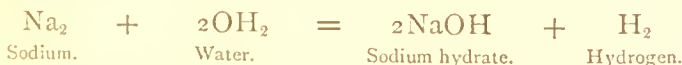Amyl nitrite.   Sulphur dioxide.   Amyl sulphate.   Nitric oxide.

Many cases of precisely the same character are not easy to find. The fact is, the great majority of reactions belong to the next class of *double* decompositions. Even some which seem to be single decompositions must in strictness be so considered ; thus, the decomposition of hydrochloric acid by sodium must be represented in this manner—

      Na Na $+$ HCl $+$ HCl
or Na_2 $+$ $2HCl =$ $2NaCl + H_2$,
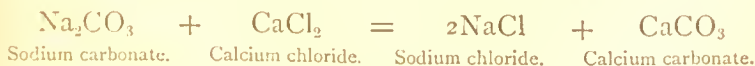not   Na $+$ $HCl =$ $NaCl + H$.
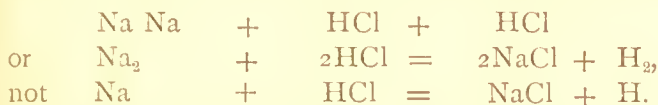
V. *Double Decomposition, or Metathesis.*—This is by far the most general mode of reaction. Two or more molecules coming together exchange some of their constituents so as to give rise to the same number, or to a greater number of molecules. We may, for the sake of completeness, classify double decompositions under three divisions :—

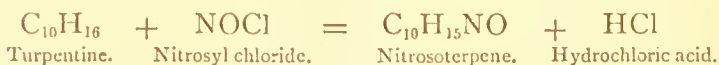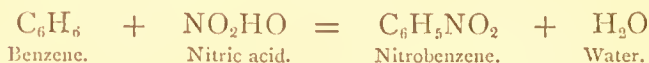1. Those in which one of the reacting bodies is an element ; e.g.,

$$Na_2 \quad + \quad 2OH_2 \quad = \quad 2NaOH \quad + \quad H_2$$
Sodium.   Water.   Sodium hydrate.   Hydrogen.

2. Those in which both are compounds ; e.g.,

$$Na_2CO_3 \quad + \quad CaCl_2 \quad = \quad 2NaCl \quad + \quad CaCO_3$$
Sodium carbonate.   Calcium chloride.   Sodium chloride.   Calcium carbonate.

3. Those which result in the formation of " substitution " compounds. This kind of reaction is not essentially different in its nature from cases 1 and 2, but substitution products among carbon compounds constitute

a class of bodies so remarkable in their characters as to deserve special notice. Some examples of their formation are given in this place, more particular mention being re- served for a later chapter.

Examples.

$$CH_4 \quad + \quad Cl_2 \quad = \quad CH_3Cl \quad + \quad HCl$$
Methane.   Chlorine.   Chloromethane.   Hydrochloric acid.

$$C_6H_6 \quad + \quad NO_2HO \quad = \quad C_6H_5NO_2 \quad + \quad H_2O$$
Benzene.   Nitric acid.   Nitrobenzene.   Water.

$$C_{10}H_{16} \quad + \quad NOCl \quad = \quad C_{10}H_{15}NO \quad + \quad HCl$$
Turpentine.   Nitrosyl chloride.   Nitrosoterpene.   Hydrochloric acid.
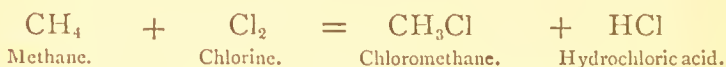
CHAPTER XI.

CHEMICAL COMPOUNDS DISTINGUISHED FROM MIXTURES.

WHEN two bodies unite together to form a chemical com- pound, they merge so completely one into the other as to be no longer recognisable by any physical character. The properties of chemical compounds are always quite distinct from those of their constituents, and in general have not even a remote resemblance to them. In the glistening red crystalline powder called by chemists mercuric oxide and vulgarly " red precipitate," no trace can be detected by the eye, or by any other sense, of the liquid, volatile, silvery metal mercury, and the colourless, gaseous oxygen into which it is resolved by the action of heat. In water, again, whether examined in the condition of solid ice, liquid water, or vaporous steam, we should look in vain for any re- semblance to the gaseous, unliquefiable elements, hydrogen and oxygen, of which it consists. Neither can we detect in the properties of water any that can be regarded as inter- mediate between those of the two constituents, or such as we should expect to find exhibited by a mixture in which each element retained its independence.

The law of definite proportions furnishes another criterion by which the character of a body under examination may be judged as to its title to rank as a definite chemical species. In order to decide whether a given substance is a true chemical compound or a mere mechanical mixture, various considerations are employed by chemists, the nature of which depends very much upon the circumstances of each particular case. If a solid body is the subject of investigation, it is examined under a microscope, in order to see if its appearance is uniform throughout ; or, if crystallisable, it is recrystallised, and the crystals compared with those of the original substance. If soluble in any liquid, it may be treated with a quantity of the solvent insufficient to take up the whole. The part dissolved, after getting rid of the solvent by evaporation or otherwise, ought to agree in every respect with the undissolved portion, if the original body is one compound and not a mixture.

In the case of those liquids which are volatile, and which bear the application of heat without decomposition, the boiling point should remain constantly at the same temperature during the distillation of the whole, and portions taken from the retort and from the distillate in the receiver ought, in the case of definite compounds, to correspond in specific gravity and all other physical and chemical characters.

When the body to be examined is a gas, the action of solvents is tried ; and if, after such treatment, the relative proportions of the ingredients are undisturbed, the body may be regarded as probably consisting of one compound. This may be confirmed by observing whether these proportions agree with the combining weights of the elements present. The phenomena of gaseous diffusion are not unfrequently useful in helping to decide whether the elements in a given gas are chemically combined or mechanically mixed. Other means of a mechanical nature may be resorted to in special cases, and occasionally considerable ingenuity is called for in devising methods suited to the occasion.

One or two examples will render these matters more intelligible to the student. We will select cases in which the law of definite proportions would afford no assistance in the solution of the problem.

Fifty-six parts of iron would unite with thirty-two parts by weight of sulphur; but the two elements may be mixed together in the state of fine powder, without exerting upon each other any chemical action whatever, the compound, ferrous sulphide, which would be formed by their union in these proportions being produced only when they are strongly heated together. The *mixture* of these two bodies, though it might be indistinguishable from the compound by appealing to the proportions of the two ingredients, would yet be easily recognised by such properties as the following:—Under a microscope particles of iron and particles of sulphur would be visible; a magnet would withdraw the iron from the powder, and leave the sulphur; carbon bisulphide would dissolve the sulphur, but would not affect the iron; a separation could be effected by merely stirring up in water, when the iron, by reason of its greater specific gravity, would sink quickly to the bottom, leaving the sulphur suspended; diluted sulphuric acid poured upon the mixture would evolve hydrogen gas. The chemical *compound* has a uniform appearance under the microscope; if reduced to powder, it could not be divided into two different portions by the use of a magnet, by any solvent, or by elutriation with water; and, lastly, the action of diluted sulphuric acid would result in the evolution of hydrogen sulphide gas, easily distinguishable from hydrogen by its odour, by its solubility in water, and by many other properties.

The domain of organic chemistry supplies numerous problems of the kind we are considering.

In certain kinds of tartar there exist the potassium salts of two acids, which have the same composition, but somewhat different properties. These acids are called respectively tartaric and racemic acids. The former rotates the

plane of polarisation of a ray of polarised light to the right, whilst the latter is optically inactive. Crystals of tartaric acid are permanent in the air, whilst those of racemic acid contain a molecule of water, which, escaping at ordinary temperatures, renders the crystals efflorescent. Racemic acid and calcium racemate are decidedly, though not very greatly, less soluble than the corresponding tartaric acid and calcium tartrate. Hence it will be perceived that whilst it is perfectly easy to distinguish the pure acids from each other, the mere estimation of the amount of carbon and hydrogen, or even an examination of a great many of the salts, would not suffice to decide between the one or the other of them and a mixture of the two.

A mixture of alcohol, water, and ether might be made in such proportions (46 : 18 : 74) that it would possess exactly the same composition as alcohol. But such a mixture would be at once distinguished from alcohol by its peculiar odour, and by separating into two layers on addition of water. When distilled, it would be found to boil at a much lower temperature than the boiling-point of alcohol ; and after about three-fourths had passed over into the receiver, the liquid left behind in the retort would no longer smell of ether, and would be easily recognised as weak alcohol.

Again, the commercial liquid alkaloid toluidine, is an oil which, when distilled, boils steadily at about 200°, and no difference of composition can be detected between the first portions of the distilled liquid and the last. And yet this substance is a mixture of two alkaloids of the same composition, one liquid, the other solid, the boiling points of which (200° and 198°) differ so slightly that they cannot be separated by any kind of fractional distillation. The only process by which they can be completely separated depends upon the fact that the oxalate of solid toluidine is much less soluble in ether than the oxalate of the liquid base. By patient repetition of this treatment with ether two

salts are obtained, which, when recrystallised any number of times, undergo no further change in crystalline form and solubility. In this condition they are believed to be pure and homogeneous.

Examples of mixtures of gases, presenting the same composition as true chemical compounds, might be easily multiplied. Thus, equal volumes of hydrogen and chlorine constitute a gaseous mixture which exhibits the colour and bleaching action of chlorine ; and after shaking up with solution of soda, just one half its bulk of colourless in- flammable hydrogen remains.

Hydrochloric acid gas, which contains the same elements combined in the same proportions, is, on the contrary, a colourless gas which no longer possesses the bleaching power of chlorine, and is readily and completely soluble in water or in solution of soda.

Ethane and hydrogen gases in equal volumes furnish a mixture which would be indistinguishable from marsh-gas by ordinary quantitative analysis. But recollecting that ethane is more than four times more soluble in water than hydrogen, whilst the rate of diffusion of hydrogen is nearly four times that of ethane-gas, it would not be difficult to distinguish the mixture from the compound. Further assistance might be derived from a study of the action of chemical agents upon the two gases.

The case of atmospheric air is one of so great impor- tance, that its consideration demands some attention in this place.

Neglecting accidental constituents, as well as the water vapour, and carbonic dioxide, which are always present, the analysis of air from various localities has led to the conclu- sion that it consists almost uniformly of 20·9 volumes of oxygen, with 79·1 volumes of nitrogen. The question whether these two elements are united together chemically has been decided in the negative, in accordance with such considerations as the following :—

1. The most accurate analyses seem to indicate that the proportion of oxygen to nitrogen in the atmosphere is not absolutely uniform, as would be the case if it were a compound.

2. The quantities of oxygen and nitrogen present do not bear any simple relation to the combining weights of those elements.

3. When oxygen and nitrogen are mixed together they show no signs of chemical action by evolution of heat or contraction of volume ; and such a mixture, when due proportions are employed, resembles atmospheric air in every respect.

4. Water dissolves the constituents of the air in unequal proportions, so that by reason of the greater solubility of oxygen, the air which may be expelled from common water by boiling contains a larger proportion of that element than is present in atmospheric air.* A chemical compound would dissolve, as a whole, without change of composition.

5. When the rays emitted from a given source of heat are transmitted through different gases, it is found that compounds absorb a much larger amount than elementary gases or mixtures of elementary gases. Thus the amount of radiant heat absorbed by nitrous oxide, a colourless and transparent gas, is more than 350 times as great as the amount absorbed by a column of equal length of oxygen, nitrogen, or atmospheric air. Between the absorbent powers of the last three gases no difference can be detected, and the natural inference, therefore, is that they are similarly constituted.

6. The elements may be separated to a certain extent by the mechanical process of diffusion through a porous plate, called, in this case, *atmolysis*.

It has also been discovered by Graham (see Chap. V., p. 31) that gases have the power of penetrating thin sheets of india-rubber, and that the rate at which oxygen passes

* See also Chapter II., p. 15, Solubility of Gases.

through this material is more than two and a-half times that of nitrogen. Upon this observation he has based a very instructive experiment, which proves conclusively the fact that the oxygen of atmospheric air is not combined with the nitrogen. An airtight india-rubber bag is ex-hausted as completely as possible by the Sprengel air-pump. When the exhaustion is nearly perfect, it is found that gas can still be slowly extracted from the bag by continuing the operation ; and this gas is found by analysis to consist of a mixture of nitrogen and oxygen, containing upwards of forty per cent. of the latter ingredient. The gases thus withdrawn from the bag result from the passage of the gases of the atmosphere through the india-rubber partition ; the oxygen, however, more rapidly than the nitrogen. The explanation of this dialytic passage of gases through the apparently impermeable caoutchouc, appears to be that the gases are absorbed by the external film of that material, that they penetrate in this condition to the other side of the sheet, where evaporation occurs in consequence of exposure to an atmosphere of very feeble density.

CHAPTER XII.

NOMENCLATURE.

A name may be used either for the purpose of indicating some particular person or object, or it may serve to point out relationships and to define the position which a thing holds in some system of classification.

In the early days of chemistry the number of different bodies known was comparatively small, and mere indicative names fulfilled all the requirements of the time. But when chemical research began to be regularly followed and crowds of new compounds were constantly presenting themselves, it became necessary to devise names which would serve, not merely to distinguish one compound from

another, but to indicate, at least in some degree, the relationship subsisting between allied bodies. The first attempts of this kind were naturally imperfect, the devices employed being wholly inadequate to the requirements of the case. For example, it soon became evident that the mere employment of adjectives, as in the names *blue*, *green*, and *white* vitriol, and the like, could have only a very limited application.

It was only after oxygen had been discovered, and its compounds were called *oxides* by Lavoisier, that chemical names began to assume some appearance of precision. The nomenclature adopted by the leading chemists of that period has met with very general acceptance ; and, although modified in detail, the system of the present day is based essentially upon the same principle. The names now employed by chemists for scientific purposes sometimes assume rather formidable dimensions, but unlike the fanciful names in use in connection with some branches of natural history, every syllable has a significance of its own. And, in spite of their length and frequent uncouthness, it may fairly be claimed for these names that they are in few cases inconvenient practically, whilst they do very fairly realise the idea originated by Lavoisier, namely, that of representing, as by a formula, the composition of the bodies for which they stand.

Nevertheless, many of the old names dating their origin from the times of the alchemists have become, by long familiarity, so incorporated into the language of medicine, of commerce, and the arts, that it is neither possible nor advisable for the chemist to reject their use. In the majority of cases, indeed, they are very serviceable, and no chemical student should disdain to make himself acquainted with such terms as *caustic potash, alum, borax,* or *oil of vitriol, wood-spirit* or *marsh-gas,* and to use them when they express all that is required, alternatively with the more formal and systematic names, the employment of which, for certain

purposes, has been rendered necessary by the advance of knowledge.

Names of Elements.—Several of the metals—-iron, copper, lead—were known in very early times. Those elements which have been discovered by more modern chemical research have received names which in some cases recall their origin, *e.g.*, silicon (silex, flint) ; whilst others were suggested by some prominent characteristic, *e.g.*, chlorine (χλωρὸς, green), or by their chemical relations, real or supposed, *e.g.*, oxygen (ὀξὺς, acid ; γεννάω, I generate).

Metals which have been discovered in modern times have all been designated by Latinised names, with the termination " ium " *—potassium, sodium, lithium, thallium, &c.; whilst the names of the non-metallic elements are characterised by no syllable which is common to them all.

Names of Binary Compounds.—When two elements are combined together, the last syllable or two of the name of one of them is changed into the suffix—ide. Thus, we have CaO, calcium oxide ; HCl, hydrogen chloride ; PbS, lead sulphide. In nearly all cases it is the name of the more negative or chlorous element which is thus modified, the name of the metal or corresponding element remaining unaltered.

Prefixes from the Greek—mono-, di-, tri-, &c.—serve to indicate the number of atoms of the chlorous element present in a molecule of the compound. Thus—

N_2O	is	nitrogen monoxide.
N_2O_2	,,	nitrogen dioxide.
N_2O_3	,,	nitrogen trioxide.
N_2O_4	,,	nitrogen tetroxide.
N_2O_5	,,	nitrogen pentoxide.

* Unfortunately this termination has been erroneously applied to the name of the non-metal selenium from a belief entertained at the time of its discovery that it was a metal. I have ventured in these pages to change the final syllable into *on*, selenion. The alteration of the name silicium into silicon within the last few years will, I hope, be considered sufficient precedent.

Not unfrequently, however, when the actual number of atoms is doubtful, or when it is desired simply to indicate a relation between two compounds, that which contains the larger proportion of the chlorine or oxygen or similar substance is distinguished by the suffix *ic*, whilst the other ends in *ous*. Thus, in the foregoing series, we may distinguish :

> N_2O as nitr*ous* oxide.
> N_2O_2 or NO as nitr*ic* oxide.

Similarly—

> N_2O_3 is nitr*ous* anhydride.
> N_2O_5 is nitr*ic* anhydride.

A few other marks serve in special cases, thus, Fe_2O_3, Cr_2O_3, Mn_2O_3, Al_2O_3, are often called *sesqui*oxides.* When there is a series of oxides, chlorides, or sulphides of the same elements, the syllables *proto*† and *per*‡ are sometimes prefixed to the name to indicate respectively the poorest and the richest in oxygen, chlorine, or sulphur, as the case may be. Thus, the two oxides of iron, which are usually represented by the formulæ FeO and Fe_2O_3, may be distinguished by one or other of the following pairs of names, according as it is desired simply to indicate that the ratio of oxygen to iron is greater in the one compound than in the other ; or to imply, what is a matter of far less certainty, that so many atoms of the two elements form one molecule of the compound.

FeO, Ferrous oxide : Iron protoxide ; Iron monoxide ;
or or
Protoxide of iron. Monoxide of iron.

Fe_2O_3, Ferric oxide : Iron peroxide ; Iron sesquioxide ;
or or
Peroxide of iron. Sesquioxide of iron.

* Latin, *sesqui*, one and a half.
† Greek, πρᾶτος, the first.
‡ Greek, ὑπέρ above, over, exceeding.

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Names of Acids and Salts.—The same principles guide
the construction of the names of these compounds, and a
single example will go far towards explaining their application. It happens, in the case of chlorine, that an unbroken
succession of compounds is formed by the union of this
element with hydrogen and oxygen. These are their names
and formulæ :

HCl	.	.	Hydrochloric acid.
$HClO$	.	.	Hypochlorous acid.
$HClO_2$	.	.	Chlorous acid.
$HClO_3$	.	.	Chloric acid.
$HClO_4$	.	.	Perchloric acid.

Here, again, the terminations *ous* and *ic* serve to indicate
different grades of oxidation, whilst the prefixes *hypo* and
per respectively announce a smaller and a larger amount of
oxygen than is contained in the chlorous and chloric acids.
In the name hydrochlor*ic* acid, it is evident that the termination has nothing to do with the presence or absence of
oxygen, and this use of the termination forms an exception
to the general rule. If we consent to regard acids as salts
of hydrogen, we may write names for this series of compounds which are constructed in all respects in the same
manner as those which are applied to salts in general.

Instead of			We may write
Hydrochloric acid	.	.	Hydrogen chloride.
Hypochlorous acid	.	.	Hydrogen hypochlorite.
Chlorous acid	.	.	Hydrogen chlorite.
Chloric acid	.	.	Hydrogen chlorate.
Perchloric acid	.	.	Hydrogen perchlorate.

And here another rule must be attended to, namely,
that when the name of a salt ends in *ite*, the name of the
acid or hydrogen salt with which it corresponds terminates
in *ous*, whilst salts in *ate* are derived from acids whose
names end in *ic*.

One more example will serve to emphasise this rule :

H_2SO_3 Hydrogen sulphite or sulphurous acid.

$NaHSO_3$ Sodium-hydrogen sulphite,

                        or acid sulphite of sodium.

Na_2SO_3 Sodium sulphite,

                        or disodium sulphite (neutral).

H_2SO_4 Hydrogen sulphate or sulphuric acid.

$NaHSO_4$ Sodium hydrogen sulphate,

                        or acid sulphate of sodium.

Na_2SO_4 Sodium sulphate,

                        or disodium sulphate (neutral)

NAMES OF CARBON COMPOUNDS.

Dr. Hofmann, a few years ago, made a proposition with the object of reducing to some degree of order the confused nomenclature of the very numerous compounds of carbon and hydrogen. The number of atoms of carbon is indicated by incorporating the Latin numeral into the name and introducing a vowel into the last syllable, in order to show the proportion of hydrogen. In the following table the words methane, ethane, propane, are based upon the names of the radicles methyl, ethyl, propyl, which have long been in use and are too familiar to be discarded :—

CH_4 Methane.	CH_2 Methene.				
C_2H_6 Ethane.	C_2H_4 Ethene.	C_2H_2 Ethine.			
C_3H_8 Propane.	C_3H_6 Propene.	C_3H_4 Propine.	C_3H_2 Propone.		
C_4H_{10} Tetrane.	C_4H_8 Tetrene.	C_4H_6 Tetrine.	C_4H_4 Tetrone.	C_4H_2 Tetrune.	
C_5H_{12} Pentane.	C_5H_{10} Pentene.	C_5H_8 Pentine.	C_5H_6 Pentone.	C_5H_4 Pentune.	C_5H_2

The succeeding terms would run : sextane, septane, octane, nonane, decane, &c.

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The radicles formed from these bodies by loss of hydrogen are furnished with the termination—yl ; thus CH_3 derived from methane by removing H is called methyl, CH is methenyl, C_2H_5 ethyl, and so on.

Unfortunately, the names which have long been applied to a great many carbon compounds are in the majority of cases fanciful, and, even in allied compounds, have no relation or resemblance to one another. They generally bear some reference either to the original source of the body, or to some more or less prominent characteristic. Thus, formic acid is so called because it was originally obtained from the bodies of ants (*formica*, an ant), acetic acid because it was procured from vinegar (*acetum*). In like manner succinic acid is the acid obtained by distillation of amber (*succinum*), and lactic acid from sour milk (*lac*).

Attempts have been made to introduce some degree of system into this crowd of heterogeneous materials by restricting the use of certain terminations. Thus, the hydrocarbons of the aromatic series have names which all end in *ene*, thus, benzene, toluene, anthracene. Alcohols and bodies resembling them claim the terminal syllable *ol ;* e.g., carbinol, phenol, thymol. Basic nitrogenous bodies are represented by names ending in *ine*, thus, ethylamine, quinine, strychnine.

These conventions do serve their purpose to some extent, though the whole matter is in a condition far from satisfactory.

CHAPTER XIII.

CONDITIONS OF CHEMICAL CHANGE.—THEORIES REGARDING THE NATURE OF CHEMICAL ATTRACTION.

WE now proceed to discuss the general conditions under which chemical changes are brought about, together with some of the circumstances which have been found to modify the exercise of chemical attraction.

1. Bodies act upon each other chemically only when, according to the usual phrase, they are in absolute contact, that is to say, when they are so near to each other that the distance between them is immeasurably small.

In this respect chemical attraction differs from the forces of gravitation, electrical and magnetic induction, all of which are capable of operating through distances which are appreciable by our senses, and measurable by our instruments. On the other hand, it agrees thus far with the force to which we give the name *cohesion*, in virtue of which the molecules of bodies are held together in masses, and with *adhesion*, which causes surfaces of various kinds after being closely approximated to remain united.

2. In order that bodies may act upon each other chemically, one of them at least must be in the liquid or in the gaseous state.

That is to say, chemical action cannot proceed to any appreciable extent unless the several parts of the acting masses are free to move, so that the mutual interpenetration which chemical combination involves may not be interfered with.

3. Moderate elevation of temperature generally favours chemical combination, and is very frequently indispensable.

In many cases it is obvious that heat assists merely by melting or vaporising one of the substances concerned; and when it gives no assistance, this may always be explained by the fact that the compound which might be formed is incapable of existing in the liquid or gaseous

state, as the case may be. Thus, iron and sulphur, or carbon and sulphur, have no action on each other, unless they are heated together very strongly. On the other hand, many salts unite with water of crystallisation only at very low temperatures; and nitric oxide, which is said to be capable of forming a compound with bromine, can only do so when the liquid is kept very cold.

But in a great many cases, as in the combination of hydrogen and chlorine, or the explosion of gunpowder, application of heat to one portion of the mass is sufficient to cause the chemical disturbance in that part to be communicated to the whole. This is in reality a gradual operation, though sometimes proceeding very rapidly, and is due to the transference of the heat which is disengaged by the reaction of the first particles to the surrounding particles, and so from one part to another throughout the mass.

Many bodies which combine together with the aid of heat are separated again when the temperature is carried too high. Mercury and oxygen afford an example of this. These two elements combine together slowly when at a temperature near the boiling-point of mercury; but the oxide which is formed is decomposed again below a red heat. In general, we may say that chemical attraction and heat are opposed in their action and effects. Whilst chemical attraction causes atoms to accumulate in molecules, heat tends to separate and scatter these atoms into simpler groups. And although, as in the production of polymeric compounds, heat seems sometimes to be capable of operating in a manner the reverse of that which has been stated, it must be remembered that in all such cases decomposition takes place at higher temperatures.

4. Heat is almost always generated when chemical combination takes place; and in every case, whether heat be absorbed or disengaged, the thermal change is as definite as are the weights of the materials engaged in the transaction.

Whenever much heat is evolved, it is tolerably safe to conclude that the resulting compound is a stable one. The explanation of this appears to be, that in order to separate two bodies which are chemically combined, they must each receive as much heat as they lost when they entered into combination.

In some cases heat appears to be absorbed ; it is so, for example, when iodine combines with hydrogen, and when sulphur combines with carbon. But in such cases, after all due allowances have been made for the heat which becomes latent in consequence of the change from solid to liquid, or gas, the actual absorption of heat which is observed must be attributed to the fact that heat is used up in the decomposition of the elementary molecules which precedes, or is simultaneous with, the formation of the molecules of the compound. Thus, when hydrogen combines with iodine, the change is not simply

$$H + I = HI$$

but is, strictly speaking, a double decomposition ; thus—

$$\left. \begin{matrix} H \\ H \end{matrix} \right\} + \left. \begin{matrix} I \\ I \end{matrix} \right\} = \left. \begin{matrix} H \\ I \end{matrix} \right\} + \left. \begin{matrix} H \\ I \end{matrix} \right\}$$

Now, if the heat required to effect the separation of H from H and I from I is greater than the amount of heat generated when $2H$ combines with $2I$, then the result will be negative, no heat will be given out, but a certain amount must be supplied from external sources.

If we compare together the thermal effects of causing one gram of hydrogen to unite with equivalent quantities of chlorine, bromine, and iodine, we get the following numbers :—

    H + Cl evolves   .   .   22000 heat units*
                                 (difference 13560)

* One unit of heat is in this case the amount of heat required to raise the temperature of one gram of water from $0°$ to $1°$.

H + Br evolves	.	.	8440 heat units
			(difference 14480)
H + I *absorbs*	.	.	6040 heat units.

These results agree with what we know of the chemical behaviour of these elements. Chlorine displaces bromine, and bromine displaces iodine from combination with hydrogen and the metals. Hydrogen, also, burns readily in chlorine gas, but with great difficulty in bromine vapour, unless mixed with air; whilst with iodine, hydrogen will unite only when strongly heated with it. In the thermal differences given above we may also observe that iodine is more widely separated from bromine than is bromine from chlorine, and this corresponds with the well-known peculiarities of iodine, which, to some extent, isolate it from the other two elements.

5. Not only is heat generated when chemical action occurs, but in at least a great number of cases a definite amount of electricity is developed. Imagine a plate of zinc plunged into a solution of hydrochloric acid. The chlorine unites with the zinc, and leaves the hydrogen to escape in bubbles from the surface of the metal. If now a plate of platinum, which is not acted upon by hydrochloric acid, is immersed in the same liquid, and connected with the zinc by a wire, it will be observed that the hydrogen is no longer disengaged from the zinc plate, but collects upon the platinum in bubbles which rise to the surface of the liquid. If the wire is cut in two, that part which proceeds from the zinc can be shown, by a gold-leaf electroscope, to be charged with negative electricity, whilst the wire from the platinum is positive. If these wires are then attached to platinum plates dipping into a solution of some salt, such as iodide of potassium, which is easily decomposable, the elements of the salt are separated, the metal going to the electrode or terminal connected with the zinc or negative pole, and the non-metallic element making its appearance at the

electrode belonging to the platinum plate* of the battery that is, at the positive pole. This process of decomposition by the voltaic current is called " electrolysis." It deserves to be noticed that it can only take place when the body to be operated upon is in the liquid state. Now, just as the amount of heat evolved by a given chemical combination is definite and constant under the same circumstances, so the electrical effect produced by contact of the same bodies under the same circumstances is constant. When electrolysis occurs in the body through which the current is passing, the quantities of its constituents which are liberated are always proportional to their chemical equivalents, and, provided secondary actions are guarded against, these quantities are also chemically equivalent to the materials consumed in each cell of the battery. If, for example, in each cell $32\cdot5$ grams of zinc are dissolved, the current passing simultaneously through solutions of iodide of potassium, bromide of potassium, acidulated water, and sulphate of copper, would set free in the

1st Cell,	127	grams of	iodine,	39·1	grams of	potassium.†
2nd "	80	"	bromine 39·1	"		"
3rd "	8	"	oxygen, 1	"		hydrogen
4th "	8	"	oxygen, 31·75	"		copper

The power of effecting electrolytic decomposition ex˜ hibited by different combinations of metals and liquids depends entirely upon the chemical characters of those bodies. The more energetic the chemical action the more powerful will be the electro-motive force of the combination. Chemical action is therefore closely connected with electricity as well as with heat.

* The elements which make their appearance at the negative pole are often referred to as *electro-positive*, whilst those which collect at the positive pole are *electro-negative*. The metals are generally electro-positive, the non-metals electro-negative.

† Hydrogen and caustic potash would, of course, be the actual products.

We have now to consider the influence of certain physical conditions in modifying the chemical action of bodies on one another.

6. When chloride of calcium and carbonate of ammonia are dissolved in separate portions of water, and the solutions are then mixed together, a precipitate of carbonate of calcium is thrown down, and chloride of ammonium remains in the mother liquid. But if these two salts, calcium carbonate and ammonium chloride, are mixed together in the dry state and heated, a decomposition occurs which is the reverse of the last, and by which the original compounds, chloride of calcium and carbonate of ammonia, are regenerated.

Again, if acetic acid is poured into an aqueous solution of potassic carbonate, effervescence ensues from the escape of carbonic acid gas, and a solution of potassium acetate is formed. But if potassium acetate is dissolved in strong spirit of wine, a liquid in which carbonate of potassium is insoluble, a stream of carbonic acid gas transmitted through the solution is capable of decomposing the acetate, throwing down a precipitate of potassium carbonate.

Experiments of this kind, which might easily be multiplied, show us that the character of a chemical reaction is very largely dependent upon the circumstances under which the operation is performed, so that a reaction which, under one set of conditions, takes place in a particular manner may be reversed when those conditions are suitably altered.

We may accept it as very generally, though not quite universally, true, that when we mix together two soluble salts, which by double decomposition are capable of giving rise to an insoluble compound, that insoluble compound will be precipitated until complete decomposition of one or both the generating salts has taken place. If, for example, we take the two salts, barium chloride and sodium sulphate, knowing beforehand that barium sulphate is insoluble in water, we may

safely assert that a precipitate will be formed when the aqueous solutions of these two salts are mixed together.

Similar observations hold good with regard to mixtures of compounds which, amongst them, contain the elements of a gas or body volatile at the temperature of the experiment. In every case this volatile body is formed. Conversely, if we submit to pressure or to a very low temperature a mixture of substances which, under ordinary atmospheric conditions, evolves a gas, the chemical action is retarded, or sometimes prevented altogether.

7. When several bodies capable of acting on one another are mixed together, but the quantity of one of them largely preponderates over the rest, some curious results are frequently brought about. When, for example, a solution of bismuth or antimony chloride in hydrochloric acid is mixed with a little water, no change is perceptible to the eye, but the addition of a larger quantity of water throws down a white precipi- tate of the oxychloride, BiOCl or SbOCl. These decompo- sitions take place according to the following equations :—

$$BiCl_3 \ + \ OH_2 \ = \ BiOCl \ + \ 2HCl$$
$$SbCl_3 \ + \ OH_2 \ = \ SbOCl \ + \ 2HCl$$

That is to say, one molecule or 18 parts by weight of water decompose one molecule or 316·5 parts of bismuth chloride or, 228·5 parts by weight of antimony chloride ; and yet, if these proportions of the materials are brought into contact, only a partial decomposition takes place, and the reaction is completed only when a much larger quantity of water is added. In such a change as this we must remember that there are two antagonistic agents at work, namely, the water tending to decompose the chloride ac- cording to the equations given above, and the hydrochloric acid which is generated by that decomposition tending to reproduce the chloride. We may, therefore, consider that there are four bodies in presence of one another, and surrounded by water molecules.

Taking one case,

$$\text{We have } BiCl_3, \ OH_2, \ BiOCl \text{ and } HCl.$$

We may safely assume that when the number of water molecules present is augmented, the number of molecules of chloride decomposed by water in a given interval will increase, whilst the number of oxychloride molecules decomposed by the hydrochloric acid present will *pari passu* diminish, until the whole of the chloride is destroyed and precipitation is complete.

If now to the liquid holding the precipitate in suspension we add hydrochloric acid in excess the action is reversed, and the precipitate disappears again.

In such experiments as these the decomposition seems to proceed continuously as the quantity of the acting body is increased, any alteration in the proportions, however small, apparently producing a corresponding alteration in the extent to which decomposition takes place.

8. Experiments made by Bunsen show, however, that this is not always the case.

When carbonic oxide and hydrogen are exploded with a quantity of oxygen not sufficient to burn them completely, the oxygen divides itself between the two gases in such a manner that the quantities of carbonic anhydride and water produced stard to one another in a simple atomic proportion. The results of Bunsen's experiments are given in the following table, the numbers in which denote volumes :—

Composition of Gaseous Mixture.			Quantities of CO and H. consumed by detonation.		Ratio of CO to H.
72·57 CO	18·29 H	9·14 O	12·18 CO	6·10 H	2 : 1
59·93	26·71	13·36	13·06	13·66	1 : 1
36·70	42·17	21·13	10·79	31·47	1 : 3
40·12	47·15	12·73	4·97	20·49	1 : 4

The results were the same whether the explosion took place in the dark, in diffused daylight, or in sunshine, and

were not affected by the pressure to which the gaseous mixture was subjected.

From these and similar results, Bunsen deduces the two following remarkable laws*:

" I. When two or more bodies B, B' . . . are presented in excess to the body A, under circumstances favourable to their combination with it, the body A always selects of the bodies B, B', &c., quantities which stand to one another in a simple atomic relation, so that for 1, 2, 3 . . . . atoms of the one compound there are always formed 1, 2, 3 . . . . atoms of the other ; and if in this manner there is formed one atom of the compound A B' in conjunction with an atom of A B, the mass of the body B may be increased relatively to that of B', up to a certain limit, without producing any alteration in the atomic proportion.

" II. When a body, A, exerts a reducing action on a compound BC, present in excess, so that A and B combine together and C is set free ; then if C can, in its turn, exert a reducing action on the newly-formed compound, AB, the final result of the action is that the reduced portion of BC is to the unreduced portion in a simple atomic proportion."

In this case, again, the mass of the one constituent may, without altering the existing atomic relation, be increased to a certain limit, above which that relation undergoes changes by definite steps.

9. We gather from the foregoing considerations that chemical attraction or affinity † is the effect of a force *sui generis,* presenting peculiarities which distinguish it decisively from the rest of the physical forces with which we are acquainted. The distinguishing characteristics of chemical attraction, briefly recapitulated, seem to be as follows :

* Watts' Dictionary, i. 860, to which the reader is referred for further details of experiments upon the influence of mass.

† The word affinity seems to have arisen from a notion current among the early chemists, that when two bodies are capable of combining, there must be some resemblance or affinity between them, or that they contain some principle common to them both.

It operates only at inappreciable distances, the weights of the reacting masses being definite and invariable for the same substance. It is also, like ordinary adhesion, elective. In other words, a given element seems, as it were, to choose between two other elements presented to it, or to leave one element in order to combine with another, as when cinnabar is decomposed by metallic iron. Lastly, the manifestation of chemical attraction through the attendant phenomena of heat, light, and electricity, is directly related, in a quantitative manner, to the performance of mechanical work.

Whatever may ultimately be concluded as to its real nature, one thing is clear, namely, that it is in some way intimately connected with motion of one kind or other in the bodies concerned.

But in entering upon the discussion of this question regarding the real nature of chemical action, it must not be forgotten that we are venturing into a region which belongs entirely to conjecture, and is—at least, at present— altogether beyond the reach of observation. From the very nature of things, no experimental test can be applied to any hypothesis that may be framed in the hope of explaining it. The student will therefore bear in mind that any suggestions that may be met with in these pages, in connection with this or kindred topics, must be accepted with all the reserve which the obscurity of the subject demands.

As already explained (in Chap. I. and elsewhere), there are good reasons for believing that the molecules of liquids and gases subsist unceasingly in a state of motion. Their agitation is increased by heat, diminished by cold. In the course of this dance in which they are engaged, and the numerous encounters which must occur amongst them, it is conceivable that some of the molecules get broken up into atoms or atomic groups, which for a while wander about until they encounter some other atom or atomic group with

which they can unite. If the original body was homo-
geneous, the molecules which are thus reproduced are of the
same kind as the original molecules. So long as this work
of reproduction goes on at the same rate as the destruction,
that is, so long as, in a given interval, the number of mole-
cules decomposed and the number of molecules recomposed
is the same, no change occurs in the properties of the body,
because the average composition of the mass remains the
same. In a mass of hydrochloric acid gas, for example, it
is conceived that if it were possible to submit it to such a
scrutiny, the greater part of the mass taken at any instant
would be found to consist of molecules, each made up of
an atom of hydrogen and an atom of chlorine; but that
with these there would be associated a certain number of
free atoms of hydrogen and chlorine interspersed amongst
them. In the next instant, many of these free atoms would
be seen yoked together again, whilst their places would be
supplied by the disruption of fresh molecules.

Now, suppose an opportunity occurs for diffusion to take
place, either into a vacuum or into another gas, the lighter
hydrogen atoms, moving much more rapidly than the
chlorine, would pass away more rapidly into the new space,
so that the residual gas would be richer in chlorine than at
first. Dissociation has not actually been observed in the
case of hydrochloric acid, but other gases and liquids
exhibit phenomena of this kind in a very remarkable
manner. (See " Dissociation," Chap. XVII.)

Or imagine this hydrochloric acid dissolved in water,
and made to perform the part of the exciting liquid in a
voltaic cell. The zinc attracts the chlorine and com-
bines with it, and the hydrogen is disengaged. Now,
it is well known, that when pure or amalgamated
zinc is used, the action goes on very slowly, but that it
proceeds with great rapidity when the circuit is completed
by connecting the two plates with a metallic wire.
This seems to indicate that the zinc does not decom-

pose the hydrochloric at all, but that it probably combines with the atoms of chlorine which it finds uncombined in the liquid. Under ordinary circumstances, these must be supposed to come into contact with it only through the operation of diffusion, and hence the process of combination is slow; but, under the influence of the electro-motive force, the dissociated atoms of chlorine are driven towards the zinc plate as fast as they become free, whilst the hydrogen atoms, under the same influence, travel in the opposite direction.

The hypothesis we are now discussing also affords an explanation of the action of mass in determining the final results of a given chemical action. The student will be able to frame the conception for himself in any given case after perusing paragraph 7.

Lastly, we may attempt to picture to ourselves the state of things which obtains when two bodies, such as hydrogen and chlorine, which have a great chemical affinity for each other, are brought together. So long as they are cool and in the dark, the process of combination is exceedingly slow, so slow, in fact, that they seem to have no action on each other. But once let the molecular agitation of even a small portion of the mixed gases be exalted to the right pitch, whether by heat or light, which is probably converted into heat, and the breaking-up of the elementary molecules proceeds rapidly throughout the entire mass, whilst new molecules of the compound, which are probably more stable than are those of either ingredient, are generated at a corresponding rate. If, however, certain limits of temperature be exceeded, the vibratory or other motion of the molecules may be sufficient to cause the disruption of increasing numbers of them until decomposition of the whole is complete.

It has been conceived that the chemical elements may be formed of the same primordial matter distributed into molecules which vibrate or rotate in different specific

periods, and that these differences of movement may correspond with the observed differences in external qualities.

Adopting such a hypothesis, it must be admitted that the molecules of a compound would almost certainly move in a manner different from the molecules of its consti- tuents. Also, that when two molecules approach each other the movement of each must be more or less modified in consequence of the proximity of the other. If the motions proper to the one are in harmony with those of the other, they may join to form a new unit moving in a different path, and consequently give rise to a body impressed with new qualities.

CHAPTER XIV.

COMBUSTION.

THE burning of wood, coal, charcoal, and other matters commonly employed as fuel, is a process with which every- one is familiar. Chemists know that the production of fire in the usual way is attended not merely by the consumption or alteration of the fuel, but by changes in the surrounding atmosphere, and that the presence of a sufficient supply of air is an indispensable condition in the operation. They explain the phenomena by stating that the process of burn- ing consists essentially in the combination of the elements of the combustible body with the oxygen in the air, so much heat being developed that more or less of the solid combustible and of the products of combustion are raised to such a temperature that they emit light. Notwithstand- ing, then, that in ordinary fires the coals disappear and seem to be destroyed, they do in reality only evaporate away in the form of carbon dioxide and water, and if these products could be collected and weighed, their weight would

be found to be made up of the united weight of the carbon and hydrogen of the coal, and the oxygen which is taken from the air.

The phenomena of combustion may be observed equally well when other materials are employed. Thus copper burns in vapour of sulphur, hydrogen will burn in chlorine, whilst phosphorus and several metals become ignited spontaneously when introduced in the proper condition into the same gas. In every such case, the resulting product consists of a compound of the body which is burned with one or other of the constituents of the gaseous atmosphere which surrounds it. From this it is evident that the terms " combustible " and " supporter of combustion," as generally employed, involve an error, if they are taken to imply any difference of function ; for that which in one experiment occupies the position of combustible, may be made the supporter of combustion or atmosphere in another. It is easy to show, for example, that not only will a jet of hydrogen burn in oxygen gas, but that a jet of oxygen burns equally well when surrounded by hydrogen.

These are the views universally accepted at the present day. They serve to account for most of the facts, though the precise explanation of the heat and light which are developed is still unknown.

Previously to the discovery of oxygen by Priestley, and the establishment of the modern theory of combustion by Lavoisier at the close of the last century, a remarkable theory had been for upwards of fifty years adopted by chemists. This was the celebrated theory of phlogiston* proposed by Stahl.† This phlogiston was supposed to be a substance of great tenuity, which, by combining with incombustible bodies, rendered them combustible. When such bodies are burnt, it was imagined that the escape of the phlogiston in a peculiar condition of vibratory motion

* φλογιστός, anything *set on fire*. † Died at Berlin, 1734.

gave rise to the phenomena of fire. At the time the idea was originally introduced, little was known of the part which the air plays in all ordinary burning. When accumulated facts proved conclusively that bodies by burning increase in weight, some attempts were made to prop up the theory by assuming that the presence of phlogiston gave bodies lightness instead of weight. The merit of the idea, however, lay not so much in providing an explanation of certain special cases of combustion, as in referring all cases of burning to a common cause, and in showing that the property of combustibility is capable of being transferred from one body to another. Oxides of the metals, for example, were regarded as ashes, or *caxles*, of the metals left after the escape of their phlogiston, which could be restored to them by contact with heated charcoal, a body which was supposed to be specially rich in the hypothetical inflammatory principle.

Whilst we believe that the presence of no substance such as phlogiston is necessary for the production of fire, and that during the manifestation of the phenomena of combustion no loss of material occurs, yet it has been very justly pointed out that bodies, when they burn, do in truth part with something, and that is the potential energy or power of doing work which belongs to a state of chemical isolation.

In order that combustion may commence in air the temperature of combustible bodies must in general be raised. The temperatures required in different cases are very diverse. Thus phosphorus, which liquefies at $44°$, can scarcely be melted in the air without inflammation. Carbon disulphide vapour mixed with air takes fire if a glass rod heated to about $150°$ is brought into contact with it. Sulphur begins to burn at about $250°$—far below its boiling point—whilst carbon and many hydrocarbons require a red heat.

The temperature produced when the process of burning is once established is in general higher than that which is

requisite for the commencement of combination. This dif-
ference is illustrated by the action of platinum upon a
mixture of hydrogen or coal gas and air. If a warm slip of
clean platinum foil or a coil of platinum wire is held in a
current of such mixed gases, the temperature of the metal
rises rapidly, in consequence of combination taking place
between those portions of the gases which are in immediate
contact with it, combination extending to the surrounding
mass only when the temperature reaches a certain point, and
the platinum is nearly white hot. Similar phenomena may
be observed in other cases when the heat evolved in the
early stages of the process is allowed to accumulate. The
spontaneous ignition of phosphorus, of finely pulverulent
iron or lead (pyrophori), and of heaps of oily rags, may
be referred to this cause.

The exact temperature of flame is difficult to determine
and is liable to vary. The temperature of a hydrogen
flame, burning in air, has been estimated at about 2080°C,
but when the flame is fed with pure oxygen its temperature
rises to upwards of 4000°C. This is easily explained by
the fact that in atmospheric air the oxygen is mixed with
four times its bulk of nitrogen, which contributes nothing to
the chemical action, and which, being raised to the same
temperature as the other gases present, consumes a great
deal of heat. A temperature still higher is produced when
a mixture of hydrogen and oxygen in due proportions is
fired in a closed vessel, so that the heated gases are not
allowed to expand. This expansion against atmospheric
pressure is work the performance of which involves the con-
sumption of heat. The temperature produced by the ex-
plosion of oxygen and hydrogen in a closed vessel has been
estimated at about 5250°C.

But although the temperatures producible by the same
combustible under various circumstances are different, the
actual amount of heat evolved in the combustion of the
same weight of a given substance is always the same. This

statement can of course be accepted only on condition of uniformity in the circumstances attending the experiment. Thus it will appear from the table given below that, as in the case of carbon, the different allotropic modifications of the same substance may give rise to appreciably different amounts of heat.

I.—Units of heat developed by combustion of equal weights of elements in oxygen.

Substance burned.	Product.	Kilograms of water heated 1°C by burning 1 kilo of each substance.
Hydrogen	Water	34034
Carbon		
a Diamond	Dioxide	7770
b Natural Graphite . . .	,,	7797
c Wood Charcoal . . .	,,	8080
Sulphur (native) . . .	Dioxide	2220
Phosphorus (common) . .	Pentoxide	5747
Zinc	Oxide	1330
Iron	Peroxide	1582

II.—Units of heat evolved by combustion of atomic weights.

Name of Element.	Weight in Kilograms.	Product.	Kilos. of water heated 1°C by the combustion.
Hydrogen . . .	1	Water (liquid) . .	34034
,, . . .	1	Hydrochloric acid (gas)	22000
,, . . .	1	Hydrobromic acid (gas)	8440
Carbon . . .			
a Diamond . .	12	Dioxide (gas) . .	93240
b Graphite . .	12	,, ,, . .	93560
c Charcoal . .	12	,, ,, . .	96960
Sulphur (native) . .	32	Dioxide (gas) . .	71042
Phosphorus (common)	31	Pentoxide (solid) .	178157
Tin ,, . .	31	Pentachloride (solid) .	107740
Tin . . .	118	Dioxide (solid) . .	135360
,, . . .	118	Tetrachloride (liquid) .	122880

The quantity of heat absolutely evolved also depends partly upon the physical condition of the products of combustion. Thus the number 34034 which expresses the heat evolved in the combination of one part by weight of hydrogen with eight parts of oxygen, represents not only the heat of chemical action, but the heat (amounting at the temperature of the experiment to about 5500 units) which is produced by the liquefaction of the resulting nine parts of steam.

This relation of the amount of heat evolved to the physical state of the resulting compounds is further indicated by the results exhibited in the following table :—

Substance burned.	Weight burned.	Product.	Units of heat evolved.
Sn	118	SnO_2	135360
SnO	134	SnO_2	$69584 \times 2 = 139168$
Cu	63·5	$C \cdot O$	38304
$CuO\frac{1}{2}$	71·5	CuO	$18304 \times 2 = 36608$
Graphite	12	CO_2	93560
CO	28	CO_2	$67284 \times 2 = 134568$

Here we find that when solid tin or copper is converted into its highest oxide, the amount of heat developed is, practically speaking, twice as great as the amount of heat developed in the conversion of the lower into the higher oxide. In other words, the two successive stages of oxidation, both of which result in the formation of solid products, are marked by the evolution of equal quantities of heat.

The case of carbon is different. In the first stage of oxidation the process involves the conversion of solid carbon into gaseous carbonic oxide, whilst in the second stage the carbonic oxide, which is burnt, and the carbonic anhydride, which is formed, are both gaseous. There is no change of state. Hence the quantity of heat which is developed in the latter operation is nearly two-thirds instead of only one-half, the total quantity evolved in

the formation of the same weight of carbonic anhydride from solid carbon.

In order, therefore, to calculate the actual amount of heat obtainable by burning a given combustible, it is necessary to take these and other circumstances into consideration. The following examples, which are unencumbered by small corrections, and in which it is assumed that no heat is lost by radiation or conduction, will serve to indicate the general nature of such calculations.

The combustion of 1 part by weight of wood charcoal evolves 8080 units of heat. That is to say, 1 kilogram of charcoal would heat 8080 kilos of water from 0° to 1°, or 1 kilo. of water from 0° to 8080°. 12 kilograms of charcoal produce 44 kilos of carbonic anhydride, or 1 kilo produces 3·67 kilos, and if the heat produced by the combustion is communicated to this quantity of carbonic anhydride, and not to water, the temperature would be $\frac{8080}{3\cdot67}$, or 2202°, if the specific heat of carbonic anhydride were the same as that of water. But the specific heat of carbonic anhydride is only ·2164, when that of water is 1. Hence, the temperature of the carbonic anhydride is $2202 \times \frac{1}{\cdot2164}$, or 10175°, when the carbon is burnt in oxygen.

Now if the combustion is performed in atmospheric air, which contains 77 per cent. of nitrogen, much heat is consumed in raising the temperature of this nitrogen.

The 2·67 parts of oxygen required for the combustion of one part of carbon are accompanied by 8·93 parts of nitrogen, the specific heat of which is ·2438. Therefore, when the combustion of carbon takes place in air, the temperature of the resulting mixture of gases cannot be higher than

$$\frac{8080}{(3\cdot67 \times \cdot2164) + (8\cdot93 \times \cdot2438)} = 2720° \text{ C.}$$

In practice, the temperature is not so high as this, partly because some heat is lost by radiation, some by conduction

through the solid unburnt charcoal, partly because an excess of atmospheric air over and above that actually required mingles with the products of combustion, and partly also because, in all probability, the specific heats are not constant, but increase as the temperature is higher.

EXERCISES ON SECTION II.

1. Give the names of the elements represented by the following symbols—Al, Sb, Fe, Mg, Hg, Mn, Ca, C, Cl, I, N, P, K, S, Ag, Na, Br, Cu, F, H, Pb, O, Si, Zn.

2. Write down the symbols and atomic weights of

        Barium, boron, bromine ;
        Calcium, carbon, copper ;
        Magnesium, manganese, mercury, silver ;
        Phosphorus, potassium, lead ;
        Sulphur, sodium, silicon ;
        Iron, iodine, chlorine, oxygen, nitrogen.

3. Read these symbols and formulæ, thus :—

N_2 represents one molecule of nitrogen, consisting of two atoms ;

O, O_2, OH_2, $2OH_2$, HCl, H_2, Cl_2, NH_3, H_3PO_4, H_2SO_4, $FeSO_4$, $2FeSO_4$, $Al_2(SO_4)_3$, $12OH_2$, $12Al_2(SO_4)_3$, CO_2, $3CO_2$.

4. Write down the formulæ and molecular weights of water, ammonia, hydrochloric acid, carbonic anhydride, sulphuric acid, ferrous sulphate, aluminic sulphate, phosphoric acid.

5. Write down the whole weight represented by each of the following expressions: $2HgO$, $10OH_2$, $3FeS$, $3FeS_2$, $2CS_2$, $KC_4H_5O_6$, $K_2C_4H_4O_6$, $5C_7H_9N$, $12CH_4$, $KAl(SO_4)_2+12OH_2$, $3[NH_4Cr(SO_4)_2+12OH_2]$.

6. Name the following compounds :—BaO, CaO, MgO, ZnS, KCl, NaBr, AgF, H_2S, HI, KCN, SSe, BN, H_3P.

7. BaO, BaO_2 ; Hg_2O, HgO ; FeS, FeS_2 ; MnO, Mn_2O_3, MnO_2 ; FeO, Fe_2O_3, Fe_3O_4 ; N_2O, N_2O_2, N_2O_3, N_2O_4, N_2O_5 ; P_2S_3, P_2S_5 ; $SnCl_2$, $SnCl_4$; $FeBr_2$, Fe_2Br_6 ; Cu_2Cl_2, $CuCl_2$; $CrCl_2$, Cr_2Cl_6, CrF_6 ; $SbBr_3$, $SbBr_5$.
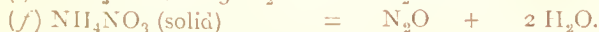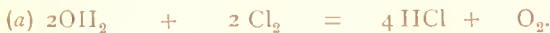
8. KNO_2, KNO_3 (—ate); K_2SO_3, K_2SO_4 (—ate); KCl, KClO, $KClO_2$, $KClO_3$ (—ate), $KClO_4$; KI, KIO_3 (—ate), KIO_4 ;

NaHSO$_3$, Na$_2$SO$_3$; Na$_2$HPO$_4$, Na$_3$PO$_4$, NaH$_2$PO$_4$; H$_3$PO$_2$, H$_3$PO$_3$, H$_3$PO$_4$ (—ic); HCl, HClO, HBrO, HClO$_2$, HClO$_3$ HIO$_3$, HClO$_4$, HBrO$_4$.

9. Write out the following equations according to the scheme on page 66—:

(a) MnO$_2$ +   4HCl   =   MnCl$_2$ +   Cl$_2$ +   2H$_2$O.
(b) 2KI   +   Cl$_2$ =   2KCl   +   I$_2$.
(c) SO$_2$ +   2OH$_2$ + Cl$_2$ = H$_2$SO$_4$ +   2HCl.
(d) NaNO$_3$ +   H$_2$SO$_4$ = NaHSO$_4$ + HNO$_3$.
(e) 2MnO$_2$ +   2H$_2$SO$_4$ = 2MnSO$_4$ + 2H$_2$O   +   O$_2$.
(f) 2K$_2$Cr$_2$O$_7$ + 8H$_2$SO$_4$ = 2K$_2$SO$_4$ +   2Cr$_2$(SO$_4$)$_3$ + 8H$_2$O
                                                       + 3O$_2$

10. Write out the following equations according to the scheme on page 67:—

(a) 2OH$_2$ +   2 Cl$_2$ =   4 HCl +   O$_2$.
(b) CO$_2$ +   C (solid) =   2 CO.
(c) 2CO   +   O$_2$ =   2 CO$_2$.
(d) 2NH$_3$ =   N$_2$ +   3 H$_2$.
(e) 2NH$_3$ +   3 Cl$_2$ =   N$_2$ +   6 HCl.
(f) NH$_4$NO$_3$ (solid)   =   N$_2$O   +   2 H$_2$O.
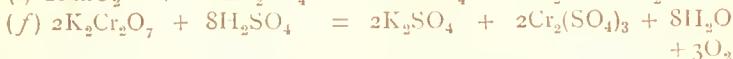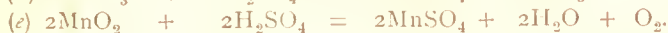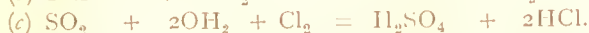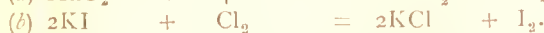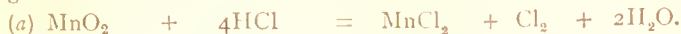
11. Write out in symbolic equations—

(a) Ammonium chloride and calcium hydrate give ammonia, calcium chloride, and water.

(b) Ammonium nitrite (heated) yields nitrogen and water.

(c) Common salt and sulphuric acid yield sodium, hydrogen sulphate and hydrochloric acid.

(d) Copper and nitric acid yield copper nitrate, nitric oxide and water.

(e) Mercury and sulphuric acid yield mercuric sulphate, sulphurous anhydride and water.

(f) Antimonious sulphide and hydrochloric acid yield antimonious chloride and sulphuretted hydrogen.

12. How many grams of oxygen are required to burn 24 grams of carbon and 32 grams of sulphur?

13. How many pounds of zinc are there in 350 pounds of the sulphate, ZnSO$_4$?

14. How much sulphur will give 100 kilograms of sulphuric acid H$_2$SO$_4$?

15. How many pounds of black oxide of manganese are required to yield, by the action of hydrochloric acid, 112 pounds of chlorine?

16. How many pounds of chalk containing 96 per cent. of calcium carbonate CaCO$_3$ will neutralise 250 pounds of sulphuric acid?

(In the following examples the gases are supposed to be at normal temperature and pressure) :—

17. Find the weight of 20 litres of oxygen, of 50 litres of chlorine, of 250 litres of ammonia.
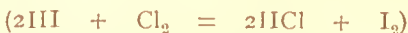
18. How many litres of oxygen are required to combine with
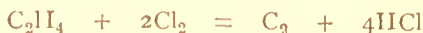
    α. 12 criths of carbon
    β. 2 grams of sulphur
    γ. 10 grams of carbon ?

19. How many litres of chlorine are required to decompose 12 litres of hydriodic acid ?

$$(2HI + Cl_2 = 2HCl + I_2)$$

20. How many litres of chlorine are required for the complete decomposition of 10 litres of olefiant gas ?

$$C_2H_4 + 2Cl_2 = C_2 + 4HCl$$

21. How many litres of hydrogen are obtained by dissolving 12 grams of magnesium in an acid ?

22. What weight of potassium chlorate is required to yield 35000 cubic centimetres of oxygen ?

23. What materials and what quantities would you employ in order to obtain 50 litres of each of the oxides of carbon ?

24. How much mercuric cyanide, $Hg(CN)_2$, must be used to furnish 50 c. c. of cyanogen, C_2N_2, assuming that 60 per cent. of the cyanogen is obtained in the gaseous form ?

25. Red oxide of copper contains 88·8 parts of copper and 11·2 parts of oxygen by weight ; black oxide of copper contains 79·87 of copper and 20·13 of oxygen. If the formula of the black oxide is CuO, how should the red oxide be represented ?

26. Water contains 88·8 of oxygen, 11·1 of hydrogen. If its formula is OH_2, find the formula for peroxide of hydrogen, which contains 94·12 O and 5·88 H.

27. Two hydrocarbons have the following composition :—

	I.	II.
Carbon	85.71	92·3
Hydrogen	14.29	7.7

$\left. \begin{array}{c} \\ \end{array} \right\} = C_2H_4$

Find the formula for II.

28. Show that the composition of the oxides of nitrogen, of manganese, and of chromium, are in accordance with the law of multiple proportion.

29. Examine the following equations, attach the name to each

formula, and classify the reactions according to Chapter X., p. 69 to
p. 71, giving reasons in doubtful cases :—

(a) Na_2 $+$ $2OH_2$ $=$ $2ONaH$ $+$ H_2

(b) Fe $+$ $H_2SO_4.H_2O =$ $FeSO_4.H_2O +$ H_2

(c) electrolysis) $2HCl$ H_2 $+$ Cl_2

(d) SO_2 $+$ H_2O_2 $=$ H_2SO_4

(e) (heat) $3MnO_2$ $=$ Mn_3O_4 $+$ O_2

(f) OKH $+$ HCl $=$ KCl $+$ OH_2

(g) O_2H_2 $+$ O_3 (ozone) $=$ OH_2 $+$ $2O_2$

(h) SO_3 $+$ H_2O $=$ H_2SO_4

(i) PH_3 $+$ $11I$ $=$ PH_4I

(j) N_2O_5 $+$ H_2O $=$ $2HNO_3$

(k) P_2O_5 $+$ $3H_2O$ $=$ $2H_3PO_4$

(l) $2KI$ $+$ Cl_2 $=$ $2KCl$ $+$ I_2

(m) C_2H_4 $+$ Br_2 $=$ $C_2H_4Br_2$
ethene

(n) $NaNO_3$ $+$ H_2SO_4 $=$ HNO_3 $+$ $NaHSO_4$

(o) (heat) $2KClO_3$ $=$ KCl $+$ $KClO^1 + O_2$

(p) MnO_2 $+$ SO_2 $=$ $MnSO$

(q) MnO_2 $+$ $2SO_2$ $=$ MnS_2O_6

(r) $C_2H_4O_2$ $+$ $3Cl_2$ $=$ $C_2HCl_3O_2$ $+$ $3HCl$

(s) K_2S $+$ CS_2 $=$ K_2CS_3

(t) C_6H_5HO $+$ HNO_3 $=$ $C_6H_4NO_2HO$ $+$ H_2O
Phenol.

(u) $C_2H_4O_2$ $+$ PCl_5 $=$ C_2H_3OCl $+$ $POCl_3$ $+$ HCl
Acetyl Chloride.

(v) $C_{10}H_{16}$ $+$ HCl $=$ $C_{10}H_{17}Cl$

(w) $3HCl$ $+$ HNO_3 $=$ $2H_2O$ $+$ NOCl $+$ Cl_2

$)x$) As_2O_3 $+$ $2HNO_3$ $+ 2H_2O$ $=$ $2H_3AsO_4$ $+$ N_2O_3

(y) (heat) $NaNH_4HPO_4$ $=$ $NaPO_3 +$ NH_3 $+$ H_2O

(z) (heat) $2Na_2HPO_4$ $=$ $Na_4P_2O_7 +$ H_2O

30. How many cubic centimetres of ammonia (measured at 15° and
under 740 mm.) would be obtained from 53½ grams of ammonium
chloride ?

31. How many cubic centimetres of sulphur dioxide (measured at 20°
and 740 mm.) can be obtained by the action of copper on 20 grams of
sulphuric acid ?

32. What weight of water would be heated from 0° to 1° by the
combustion of 1 gram of charcoal in oxygen ?

33. What weight of water would be heated from 0° to 15° by the
combustion of 1 gram of hydrogen in chlorine ?

34. Calculate the temperature of combustion of phosphorus burn-
ing in air.

35. Heat of combustion of hydrogen .   . 34034 units
    Latent heat of steam   536
    Specific heat of steam .   .   .   . ·475
    Specific heat of nitrogen .   .   .   ·2438
        Composition of air, N77, O23 parts by weight.

With these data find the temperature of the hydrogen flame burning
in air.

Answer :—

$$\frac{34034 - (536 \times 9)}{(9 \times \cdot 475) + (26\cdot 7 \times \cdot 2438)} = 2708°C.$$

SECTION III

CHAPTER XV.

EQUIVALENTS AND ATOMIC WEIGHTS.

WHEN a strip of metallic copper is immersed in a slightly acid solution of mercuric chloride the mercury begins at once to be deposited, and copper is at the same time dissolved. After the lapse of a sufficient length of time the whole of the mercury will thus be thrown down and the liquid will then contain nothing but copper chloride. When this result has been brought about it will be found that for every 100 parts by weight of metallic mercury obtained, 31·75 parts of copper are consumed.

If now a piece of iron is plunged into the solution of copper chloride the copper salt is in its turn decomposed and the whole of the metal recovered, iron being substituted for it. And if the weights of the metals which thus exchange places are determined, it will prove that in order to precipitate the 31·75 parts of copper in the liquid 28 parts of metallic iron must go into solution.

Moreover, it is found that whenever one of these metals, mercury, copper, iron, is exchanged for another, the weights concerned are always in these proportions. These quantities are then said to be *equivalent* to one another.

But, further, when iron is dissolved in hydrochloric or sulphuric acids, these 28 parts liberate from the acid one part by weight of hydrogen.

In the three compounds, hydrochloric, hydrobromic, and

hydriodic acids, 35·5 parts of chlorine, 80 parts of bromine, and 127 parts of iodine are united with 1 part by weight of hydrogen, and it is also found that when chlorine, bromine, or iodine takes the place of hydrogen, as they frequently do in carbon compounds, the quantities which replace 1 part by weight of hydrogen are represented by the same numbers.

Again, the metals mercury, copper, and iron are capable of combining with chlorine, bromine, and iodine, forming various chlorides, bromides, and iodides ; but the analysis of these compounds reveals the fact that these are all made up of their elements in proportions which may be represented as multiples of the numbers which have been found to be characteristic of the same elements in other cases. Thus there are two chlorides of iron, of which the first contains 28 parts of iron united to 35·5 parts of chlorine, whilst the second consists of 28 × 2 or 56 parts of iron, with 35·5 × 3 or 106·5 parts of chlorine.

By such observations it is established that :—

$$
\left.
\begin{array}{ll}
100 \text{ parts of mercury} \\
31\cdot75 \quad ,, \quad \text{copper} \\
28 \quad\quad ,, \quad \text{iron}
\end{array}
\right\}
\begin{array}{l}
\text{are equivalent to each other} \\
\text{and to 1 part of hydrogen.}
\end{array}
$$

And that—

$$
\left.
\begin{array}{ll}
35\cdot5 \text{ parts of chlorine} \\
80 \quad ,, \quad \text{bromine} \\
127 \quad ,, \quad \text{iodine}
\end{array}
\right\}
\begin{array}{l}
\text{are equivalent to each other} \\
\text{and to 1 part of hydrogen.}
\end{array}
$$

Also that—

$$
\left.
\begin{array}{ll}
100 \text{ parts of mercury} \\
\text{or } 31\cdot75 \quad ,, \quad \text{copper} \\
\text{or } 28 \quad\quad ,, \quad \text{iron}
\end{array}
\right\}
\quad \text{are at least sometimes}
$$

equivalent to—

$$
\begin{array}{ll}
& 35\cdot5 \text{ parts of chlorine.} \\
\text{or } & 80 \quad ,, \quad \text{bromine.} \\
\text{or } & 127 \quad ,, \quad \text{iodine.}
\end{array}
$$

The term "equivalent," or "equivalent number," was, however, formerly employed to designate the weights of the several elements, which are capable of entering into combination with one part by weight of hydrogen, and by some chemists it is still restricted to this sense.

The exact experimental determination of these combining proportions is a matter of great importance, for it is in all cases the first step towards the establishment of the atomic weights. The methods used in these determinations vary according to the nature of the elements concerned, and cannot be dwelt upon in a work of this kind.

It is unnecessary to draw up a complete list of the equivalent numbers of all the elements, because when the student has learnt by heart the atomic weights, he can always calculate the equivalents by a very simple operation. For the equivalent number, as must be obvious, bears a very simple relation to the weight of the atom, being in every case either identical with the atomic weight or an aliquot part of it.

It must be remembered, however, that in actual practice the determination of the equivalent precedes the calculation of the atomic weight, for the former is a number which is found by experiment, whilst the latter is to a certain extent hypothetical.

It has already been mentioned that in the system of atomic weights or ratios now universally employed by chemists, the atomic weight of hydrogen is taken as the unit.

The atomic weights of all the other elements are fixed by reference to one or other of the following rules.

In those few instances in which it is possible to make use of all of them, it is found that the number indicated by the application of any one of these rules is identical, or nearly identical, with the number indicated by the others. This is, of course, important, as showing that these different considerations lead to the same conclusion ; and, there-

fore, that our atomic weights belong to one and the same system.

I. The atomic weight, as deduced from other considerations, is identical in a few cases with the specific gravity of the element in the gaseous state.

This occurs in the case of the gases hydrogen, oxygen, nitrogen, chlorine, and the volatile bodies, bromine, iodine, sulphur, selenion, potassium, and probably sodium.

Mercury, cadmium, and zinc are exceptions to this rule, as well as the non-metallic elements—arsenic and phosphorus. The three former produce vapours, the specific gravities of which, as compared with that of hydrogen, are the halves of their atomic weights, whilst the vapour densities of the two last are represented by numbers which are equal to twice the atomic weights.

Name of Element.				Specific Gravity of Gas or Vapour.	Atomic Weight.
Hydrogen	.	.	.	I	I
Oxygen	.	.	.	16	16
Nitrogen	.	.	.	14	14
Chlorine	.	.	.	35·5	35·5
Bromine	.	.	.	80	80
Iodine .	.	.	.	127	127
Sulphur	.	.	.	32 (at high temps.)	32
Selenion	.	.	.	79 (do. do.)	79
Potassium	.	.	.	39 ?	39
Sodium .	.	.	.	23 ?	23
Mercury	.	.	.	100	200
Cadmium	.	.	.	56	112
Zinc .	.	.	.	32·5 ?	65
Arsenic .	.	.	.	150	75
Phosphorus	.	.	.	62	31

II. According to the system here adopted, and which will be further dwelt upon in the next chapter, the bulk of one part by weight of hydrogen is regarded as the volume of the atom of that element, and is selected as the unit for comparison of other volumes, atomic and molecular. Twice

this bulk of hydrogen contains a molecule, and all molecules in the gaseous state occupy the same volume. Now, according to the atomic theory, a molecule cannot contain less than one atom of any element ; and, consequently, if we ascertain what is the smallest quantity of an element contained in a molecule of any compound of which it may be a constituent, we shall have determined the atomic weight of the element.

The atomic weight, then, may be said to be the smallest weight of the element ever found in two volumes of the vapour of any of its volatile compounds, the bulk of one part by weight of hydrogen, at the same temperature and pressure, being considered as one volume.

Suppose, for example, it is required to find by this rule the atomic weight of oxygen, we have only to ascertain the vapour densities of a number of compounds containing that element and the weight of oxygen contained in each. The results are then tabulated in the following manner :—

Volatile Compounds containing Oxygen.	Specific Gravity, that is Weight of 1 Volume of Gas or Vapour at same Temp. and Pressure.	Weight of Two Volumes.	Weight of Oxygen contained in Two Volumes.
Water	9	18	16
Carbonic oxide .	14	28	16
Carbonic anhydride .	22	44	32
Sulphurous anhydride	32	64	32
Sulphuric anhydride .	40	80	48
Nitrous oxide	22	44	16
Nitric oxide	15	30	16
Alcohol	23	46	16
Ether	37	74	16
Acetic acid	30	60	32
Etc.	etc.		etc.

Two volumes of the vapour of any volatile compound, therefore, never contain less than 16 parts of oxygen, and hence 16 is accepted as its atomic weight.

This is a rule of very general applicability, for although a great many of the elements, carbon for example, are quite incapable of being volatilised at any manageable temperature, they yield a large number of easily volatile compounds.

There are, however, many metals which are neither vaporisable by themselves nor when in union with other elements. In such cases this rule cannot be applied, and information has to be sought in a different direction.

III. *Law of Dulong and Petit.*—" The specific heats of the solid elements are inversely proportional to their atomic weights." Whence it follows that the product of the multiplication of the specific heat by the atomic weight is a constant number.

In the following table are given the specific heats of the most important of the elements, together with their atomic weights :—

Name of the Element.	Atomic Weight.	Sp. Ht. of Equal Weights.	Sp. Ht. of Atomic Weights.
Aluminium	27·4	·2143	5·87
Antimony	122	·0508	6·20
Arsenic .	75	·0814	6·11
Bismuth .	210	·0308	6·47
Boron (crystallised).	11	·2300	2·53
Bromine (solid)	80	·0843	6·74
Cadmium	112	·0567	6·35
Carbon .	12		
α Wood charcoa .		·2410	2·89
β Natural graphite		·2020	2·42
γ Diamond .		·1469	1·76
Cobalt .	59	·1067	6·29
Copper .	63·5	·0952	6·04
Gold	197	.0324	6.36
Iodine .	127	·0541	6·87
Iron	56	·1138	6·37
Lead .	207	·0314	6·50
Lithium .	7	·9408	6·59
Magnesium	24	·2499	6·00
Mercury (solid)	200	·0319	6·38
Nickel .	59	·1092	6·44

Name of the Element.	Atomic Weight.	Sp. Ht. of Equal Weights.	Sp. Ht. of Atomic Weights.
Phosphorus	31		
α Common		·1895	5·87
β Red		·1698	5·26
Platinum	197·5	·0324	6·40
Potassium	39·1	·1655	6·47
Silicon	28		
α Graphitoidal		·1810	5·07
β Crystallised		·1650	4·62
γ Fused		·1380	3·86
Silver	108	·0570	6·16
Sodium	23	·2934	6·75
Sulphur (Octahedral)	32	·1776	5·68
Tin	118	·0562	6·63
Zinc	65	·0956	6·23

The greater number of the specific heats given in this table were determined by Regnault. A glance down the fourth column will show that, with three exceptions (boron, carbon, and silicon), the amount of heat required to produce the same change of temperature in the different elements is nearly the same in all cases when the quantities operated upon are in the proportion of their atomic weights. That the numbers representing the atomic heats are not found to be exactly identical is due partly to unavoidable errors in the estimation of the specific heats, and partly to the fact that the different elements are not dealt with under conditions which are strictly comparable with one another. Thus, solid mercury and solid bromine, at the temperatures at which the specific heats were determined, are much nearer to their melting points than are the solids, copper and iron, at the temperatures at which the same operation was performed upon them. Other circumstances, such as the assumption of different allotropic forms by some of the elements, tend to the introduction of further uncertainty.

But assuming the rule, with the exceptions already named, we find that the atomic heat of a solid element may be represented on the average by the number 6·2.

Nevertheless, since the determination of specific heats is always attended by many sources of error, whilst the equivalent or combining proportion can be fixed with a very considerable degree of accuracy, the application of this law consists essentially in enabling us to decide as to what multiple of the equivalent is to be taken as the atomic weight. In doing this, we are guided by the formula

$$\text{At. Wt.} \quad = \quad \frac{6{\cdot}2}{\text{Sp. Ht.}}$$

Suppose, for example, it is found that 29·5 parts of tin are equivalent to 1 part of hydrogen, and we require to find the atomic weight. The specific heat of tin is ·0562, therefore

$$\text{At. Wt.} \quad = \quad \frac{6{\cdot}2}{{\cdot}0562} \quad = \quad 110{\cdot}3$$

The atomic weight of tin is, however, not taken to be 110·3, but rather such a multiple of 29·5 as comes nearest to that number, and this is found to be 29·5 × 4 or 118.

IV. *Law of Isomorphism.*—If a crystal of common potash alum is immersed in a saturated solution of the purple chrome alum, the purple salt is deposited uniformly over the colourless nucleus, so that the crystal increases in bulk though it undergoes no alteration of form. The resulting crystal may be transferred to a solution of ammonia alum, or of iron, or manganese alum, and during every fresh immersion it receives a deposit of a different salt upon its surface, the crystalline form, that of the regular octahedron, being throughout preserved.

If instead of·thus causing successive layers of the various alums to be superposed one upon the other, solutions of any two of these salts are mixed together, crystals of the same form are deposited containing the elements of both salts.

The alums are double sulphates, all containing the same

amount of water of crystallisation, and having a composi-
tion which may be represented by the general formula

$$M' \ M''' \ (SO_4)_2 + 12OH_2$$
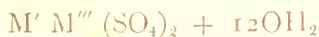
in which M' may be Cs, Rb, K, Na, Am, Tl or Ag, and
M''' may be Fe, Mn, Cr or Al.

If, therefore, any two of these compounds are compared
together, as for example

| Potash Alum | - | $KAl(SO_4)_2.12OH_2$ |
| Soda Alum | - | $NaAl(SO_4)_2.12OH_2$ |

it is obvious that atom for atom they have the same con-
stitution, but the one contains potassium, the other sodium.
This exchange of an atom of one element for an atom of
another is in this case effected without producing any altera-
tion in the crystalline structure of the resulting salt, and
when bodies thus agree in chemical constitution and in
crystalline form, they are said to be *isomorphous*.

From the examination of a great many instances of the
same kind, chemists have been led to infer that when two
bodies, composed of the same or similar elements, crystal-
lize in forms belonging to the same crystallographic system,
they generally contain the same number of atoms united
together in a similar manner.

This statement must be considered to include cases in
which groups of atoms (compound radicles) take the place
and perform the part of single elementary atoms. The
compounds of ammonia with acids, for example, are
isomorphous with the corresponding salts of potassium,
and a constitution is therefore attributed to the ammoniacal
salts similar to that of the potassic salts, the symbols NH_4
being the representative of the metal in these compounds.
Thus in the following pairs of compounds there is the most
complete concordance in chemical characters as well as in
crystalline form.

Cubical.

AmCl (Am = NH_4)   KCl.

Four or Six sided Prisms (Trimetric).

$Am_2 SO_4$ $K_2 SO_4$

Octahedral (Regular.)

$AmAl(SO_4)_2 \; 12OH_2$ $KAl(SO_4)_2 \; 12OH_2$

Am_2PtCl_6 K_2PtCl_6
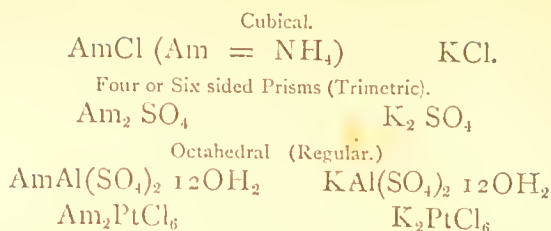
Although some of the relations between external crystalline form and chemical constitution are still involved in obscurity, the existence of a great number of well-marked cases of isomorphism is a fact which is familiar to every chemist, and occasionally the application of this principle has led to the settlement of questions relating to atomic weights, regarding which there had been previously more or less of uncertainty.

For instance, alumina, the only known oxide of aluminium, is believed to have the same constitution as ferric oxide, because not only do the oxides themselves agree in crystalline form, but they are capable of replacing each other in their compounds without disturbing the crystalline structure of these bodies. Now, since ferric oxide is universally regarded as a sesquioxide, that is, containing in each molecule two atoms of the metal to three atoms of oxygen, alumina is believed to be formed upon the same type, and if the formula Fe_2O_3 be employed to represent ferric oxide, Al_2O_3 must be admitted as the formula for alumina. If these considerations have to be applied to the determination of the atomic weight of the metal, we have only to refer to the analysis of alumina to find that 100 parts contain

53·3 parts of aluminium,

and 46·7 ,, ,, oxygen.

And since, according to the formula, we have 3×16 or 48 parts of oxygen united with $2x$ parts of metal, we can easily calculate the value of x ($= 27·4$), which is the atomic weight.

Other instances of a like character would readily present

themselves upon enquiry. The following is an interesting example :—

It is well known that the crystalline forms of sodium nitrate and calc-spar are nearly identical, and a crystal of calc-spar immersed in a saturated solution of the nitrate will grow by uniform deposition of that salt all over its surface.

But arragonite (another form of calcium carbonate) is also found in the same form as potassium nitrate. All these, facts, then tend to prove that calcium carbonate probably contains the same number of atoms as the nitrates of potassium and sodium, and that its formula should be

$$CaCO_3 \text{ if the}$$
$$\text{others are } KNO_3 \text{ and}$$
$$NaNO_3 \text{ respectively.}$$

But this formula cannot be used unless we assume that the atomic weight of calcium is 40, a number which agrees with the value deduced from other considerations.

V. In not a few cases the atomic weight selected for any element in accordance with the foregoing rules may receive support and confirmation from a study of the chemical reactions of some body containing the element in question. For example, we have evidence that in a molecule of water the hydrogen present is capable of being expelled in two equal parts by the action of the metal potassium or sodium, whilst the oxygen is not divisible in any such manner by chlorine or any other element which possesses the power of replacing it. Hence the formula H_2O.

Similar arguments might be applied in a slightly different manner. For example, 46 parts of formic acid are equivalent to 60 parts of acetic acid, since both saturate the same quantity of any base, and represent two volumes of vapour. The former contains 12 parts of carbon, the latter 24. so that, according to rule II., p. 113, we believe 46 parts of formic acid contain one atom of carbon, whilst an equivalent quantity of acetic acid contains two atoms.

Further evidence of this may be found in the fact that when formic acid is submitted to electrolysis all its carbon goes to form carbon dioxide, whilst when acetic acid is electrolysed half its carbon goes to form carbon dioxide, whilst the other half combines with hydrogen and furnishes ethane. The carbon of acetic acid is, therefore, divisible in this operation into two equal parts, whilst that of formic acid seems to be in the literal sense atomic.

CHAPTER XVI.

MOLECULAR WEIGHTS AND FORMULÆ.

WHEN a compound has been analysed, it is usual in the first instance to represent its composition by the percentages of the several elements of which it is made up. Acetic acid, for example, contains—

$$
\begin{aligned}
&\text{Carbon} & . & . & . & . & . & . & . & 40 \cdot 0 \\
&\text{Hydrogen} & . & . & . & . & . & . & 6 \cdot 6 \\
&\text{Oxygen} & . & . & . & . & . & . & . & 53 \cdot 4
\end{aligned}
$$

in 100 parts. The next step is to endeavour to write a formula which, whilst expressing the same facts more compactly, gives, at the same time, the number of atoms of the constituent elements, and fixes the relative weight of the molecule.

If the atomic weights of the elements were all equal, the formula would be a mere repetition of the percentages; but since they are different, the number of atoms of the several elements contained in equal weights must be inversely as their atomic weights.

The simplest rule for deducing the formula of a compound from its percentage composition is, therefore, to divide the respective quantities by the atomic weights of the elements.

Thus, if we divide the percentages of carbon, hydrogen, and oxygen in acetic acid by the atomic weights of carbon, hydrogen, and oxygen respectively, we arrive at these results.*

$$\frac{40}{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad = \; 3\text{·}3$$

$$\frac{6\text{·}6}{1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad = \; 6\text{·}6$$

$$\frac{53\text{·}4}{16} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad = \; 3\text{·}3$$

So that evidently there are as many atoms of oxygen present as there are of carbon, and there are twice as many hydrogen atoms. The simplest formula, then, that can be written for acetic acid is CH_2O, but whether this is to be taken as representing a molecule of acetic acid or whether the true formula is some multiple of this, such as $C_2H_4O_2$ or $C_3H_6O_3$, remains to be decided by considerations which now require to be examined.

VAPOUR DENSITY AND MOLECULAR WEIGHT.

According to the law of Avogadro (Chap. VI.), equal volumes of all true† gases, irrespective of chemical composition, contain under the same conditions of temperature and pressure the same number of molecules. It follows from this that the weights of equal volumes must be proportional to the weights of the molecules of which the gases are composed.

This is the principle of the only *direct* method for ascertaining the relative weights of these molecules.

Comparing together, for example, equal measures of hydrogen and hydrochloric acid gases, we find their respective weights represented by the numbers 1 and 18·25. But the weight of hydrogen contained in hydrochloric acid is exactly half the weight of the same element contained in an

* See Examples and Exercises, p. 165, No. 25.
† That is gases obeying the law of Boyle.

equal measure of hydrogen, and if we assume that there is one atom of hydrogen in a molecule of hydrochloric acid (and by the theory there cannot be less than one atom), we arrive at the conclusion that the molecule of hydrogen consists of at least two atoms. But, further, we have every reason to believe that whilst the molecule of hydrochloric acid contains at least one atom of hydrogen, it does not contain more than one atom. When metals act upon hydrochloric acid the hydrogen is expelled all at once, and not in several portions, as in the case of water and ammonia. So that assuming the atomic weight of hydrogen as 1 unit of weight, the molecule of hydrochloric acid must weigh 36·5 units. The weight of hydrogen equal in bulk to this, that is to say, one molecule of hydrogen or two unit volumes, must accordingly be 2.*

So that, in order to express the molecular weights of these gases, we must double their specific gravities, and this rule is applied to all gaseous and volatile bodies, with the few exceptions referred to in the next chapter.

The application of this principle to those of the elements that are volatile leads to the conclusion that many of them, like hydrogen, consist of molecules having a duplex structure, whilst examples are not wanting of a more complex as well as of a simpler constitution. We come, in fact, to the following classification :—

* The student will now perceive why 2 volumes and not 1 volume or 3 or 4 volumes is regarded as the standard volume of molecules. One volume would be inconvenient, because we find that the molecule of hydrogen can be divided into two equal parts, and this would necessitate the use of fractions. Three volumes would be incorrect, because the hydrogen molecule is divisible into two and not into three atoms. Four volumes would also be inadmissible, because the same bulk, that is one molecule of hydrochloric acid, would then be represented as containing two atoms of hydrogen and two atoms of chlorine H_2Cl_2. Whereas it is a matter of fact that neither the hydrogen nor the chlorine in hydrochloric acid is divisible into separate parts.

Monatomic Molecules :—				Molecular		
				Formula.		Weight.
Mercury	.	.	.	Hg	.	200
Cadmium	.	.	.	Cd	.	112
Zinc	.	.	.	Zn	.	65

Diatomic Molecules :—

Hydrogen	.	.	.	H_2	.	2
Oxygen	.	.	.	O_2	.	32
Nitrogen	.	.	.	N_2	.	28
Chlorine	.	.	.	Cl_2	.	71
Bromine	.	.	.	Br_2	.	160
Iodine	.	.	.	I_2	.	254
Potassium	.	.	.	K_2	.	78.2
Sulphur (at 900°)		.	.	S_2	.	64

Triatomic Molecule :—

Ozone	.	.	.	O_3	.	48

Tetratomic Molecules :—

Phosphorus	.	.	.	P_4	.	124
Arsenic	.	.	.	As_4	.	300

Hexatomic Molecule :—

Sulphur (at 500°)		.	.	S_6	.	192

Assuming, then, the equality in volume of gaseous mole-
cules, and knowing that the molecule of hydrochloric acid
contains an atom of hydrogen, the conclusion that a
molecule of this element consists of two atoms is inevit-
able. But further evidence of this fact may be obtained
from other considerations unconnected with the question
of the constitution of gases.

NASCENT STATE.

Thus, it is well known that bodies in the *nascent* state,
that is, at the instant of their liberation from compounds,
are capable of acting far more energetically than when they
are employed in the bodily form. Hydrogen *gas*, for
example, is generally incapable of combining with other

bodies ; but when materials such as zinc and dilute sulphuric acid, which are capable of yielding hydrogen, are employed, many decompositions and combinations may be brought about which would be otherwise impossible. Solution of sulphur dioxide may in this way be converted into hydrogen sulphide and water by the action of zinc and diluted hydrochloric acid, the *nascent* hydrogen attacking and combining with both the sulphur and the oxygen. An instructive experiment, illustrating the power both of nascent oxygen and hydrogen, consists in electrolysing a solution of hydrochloric acid coloured with indigo. The liquid in the neighbourhood of both poles is bleached ; at the negative, because the hydrogen there liberated combines with the indigo and forms a colourless compound ; at the positive, because the chlorine, acting on the water, disengages oxygen, which, whilst still nascent, combines with the elements of the indigo, producing a pale yellow substance. Neither oxygen nor hydrogen in the ordinary gaseous form is capable of producing these effects, which are usually supposed to be due to the superior powers of the atoms whilst still in the free state and before they have partly expended their energies by coupling in pairs or otherwise binding together in molecules.

CATALYTIC ACTIONS.

Metallic copper is incapable of expelling hydrogen from hydrochloric acid, even when boiled with it. But by adding hypophosphorous acid to a warm solution of sulphate of copper, a brown precipitate of cuprous hydride is thrown down, and this compound, in contact with hydrochloric acid, evolves hydrogen and furnishes cuprous chloride. This reaction can only be explained upon the assumption that it is *the attraction of the hydrogen in the copper hydride for the hydrogen in the acid*, superadded to that of the copper for the chlorine, which determines the metathesis :

$$Cu_2\begin{matrix}H\\H\end{matrix} \quad + \quad \begin{matrix}H-Cl\\H-Cl\end{matrix} \quad =$$
$$Cu_2\begin{matrix}Cl\\Cl\end{matrix} \quad + \quad \begin{matrix}H-H\\H-H\end{matrix}$$
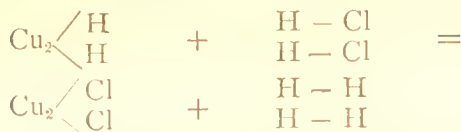
A great many reactions of a similar character are known chiefly among compounds containing a relatively large proportion of oxygen, part of which escapes in the gaseous form. Thus, when silver oxide is placed in contact with peroxide of hydrogen, the silver is reduced to the metallic state, water is formed, and oxygen gas evolved.

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2$$
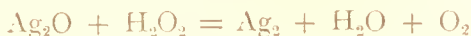
In like manner, permanganic and chromic acids are decomposed by peroxide of hydrogen with evolution of oxygen gas ; and in these and similar reactions it has been proved experimentally that half the oxygen comes from the peroxide, half from the acid or other body with which it is in contact. The conclusion seems inevitable that these two halves of the oxygen had an attraction for each other which was sufficient to upset the equilibrium of the unstable compounds of which they previously formed a part.

SYNTHETICAL PRODUCTION OF MOLECULES.

The cases that we have hitherto had under discussion have been chiefly those of the elements. If we have to examine into the constitution of compounds, we have yet several sources of information which will help in the solution of the problem of their molecular weights and formulæ. One very important kind of argument is deduced from a knowledge of the mode or modes in which the compound may be formed, and of the products of its decomposition under the influence of reagents.

For example, oxalate of sodium is formed when carbonic anhydride gas is passed over heated sodium. The change, however, might be represented by either of the following equations :—

$$Na + CO_2 \quad = \quad NaCO_2$$
$$or, \quad Na_2 + 2CO_2 \quad = \quad Na_2C_2O_4$$
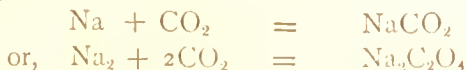
But the doubt, if there were any, would be resolved in favour of the latter alternative, by the observation that when sodium oxalate is heated it yields carbonic oxide gas, leaving a residue of carbonate.

$$Na_2C_2O_4 = \left\{ \begin{array}{l} CO \\ Na_2\,CO_3 \end{array} \right.$$

The most direct and rational explanation of this is, that a molecule of the salt contains two atoms of carbon, as represented by the formula.

Again, succinic acid may be built up from its elements by a succession of processes, which are briefly represented in the following series of equations, and from them we learn, even if no other evidence were forthcoming, that succinic acid contains at least four atoms of carbon in a molecule, and hence must have the formula here assigned to it.

Carbon poles ignited by the electric current in hydrogen gas give rise to acetylene.

$$C_2 + H_2 = C_2\,H_2$$
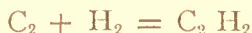
Acetylene can be made to combine with hydrogen yielding ethylene, the known specific gravity of which gas renders impossible any doubt as to its molecular weight.

$$C_2H_2 + H_2 = C_2H_4$$
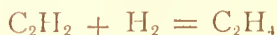
Ethylene combines with bromine thus,

$$C_2H_4 + Br_2 = C_2H_4Br_2$$
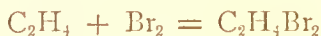
This dibromide may be converted into a cyanide,

$$C_2H_4Br_2 + 2KCN = C_2H_4C_2N_2 + 2KBr.$$

Lastly, this cyanide, under the influence of boiling alkali, assimilates the elements of water, and yields up its nitrogen in the form of ammonia.

Cyanide of ethylene.   Potassium succinate.

$$C_2\,H_4\!\left\{ \begin{array}{l} CN \\ CN \end{array} \right. + 2KHO + 2H_2O = C_2H_4\!\left\{ \begin{array}{l} CO_2K \\ CO_2K \end{array} \right. + 2NH_3$$
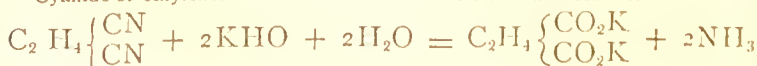
From this salt the acid may be procured by the action
of sulphuric acid.

$$C_2\,H_4\begin{Bmatrix}CO_2K\\CO_2K\end{Bmatrix} + \begin{Bmatrix}H\\H\end{Bmatrix}\,SO_4 = C_2H_4\,(CO_2H)_2 + K_2SO_4$$

<div align="center">

Potassium   Sulphuric   Succinic   Potassium
succinate.   acid.   acid.   sulphate.

</div>
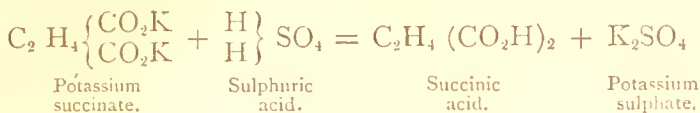
SATURATING POWER OF ACIDS AND BASES.

In the examination of acids and bases, and other bodies.
which are capable of entering into combination readily, or
of suffering the replacement of some of their elements by
simple reactions which do not involve destruction of the
molecule, the process for determining the molecular weight
is generally easy. Suppose, for instance, it is required to
determine the molecular weight of sulphuric acid, it is only
necessary to add to it various quantities of potash or soda
to discover that there are two, and two only, distinct and
definite sulphates of potassium and sodium, and that
even double salts are possible, in which the two metals
figure side by side, in place of the hydrogen of the acid.
So that sulphuric acid and its salts are representable by
such formula as the following :—

$$\begin{Bmatrix}H\\H\end{Bmatrix}SO_4 \quad \begin{Bmatrix}K\\H\end{Bmatrix}SO_4 \quad \begin{Bmatrix}K\\K\end{Bmatrix}SO_4$$

$$\begin{Bmatrix}K\\Na\end{Bmatrix}SO_4$$

$$\begin{Bmatrix}Na\\H\end{Bmatrix}SO_4 \quad \begin{Bmatrix}Na\\Na\end{Bmatrix}SO_4$$
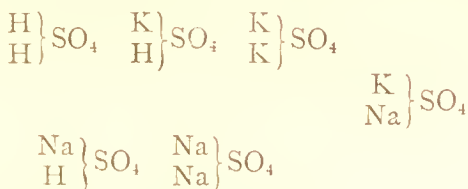
Basic derivatives of ammonia are dealt with in a similar
way. If we assume that the molecule of hydrochloric acid
is represented by the symbols $HCl(= 36\cdot5)$, the problem
is to find what weight of base will enter into combination
with $36\cdot5$ parts of hydrochloric acid so as to produce a
neutral compound. In the case of ammonia itself, the
compound formed with hydrochloric acid is represented by
the formula NH_3HCl, in which NH_3 stands for 17 parts
by weight of ammonia. In some cases, it is practically

more convenient to prepare the double salts which the hydrochloride of ammonia and all similarly constituted compounds form with platinic chloride. Ammonio-chloride of platinum has the formula $2(NH_3 \cdot HCl).PtCl_4$, and that quantity of the basic body which, in this compound, is capable of taking the place of ammonia, NH_3, is generally* taken to be its molecular weight.

SUBSTITUTION COMPOUNDS.

In other cases, especially when the compound under examination is neutral, and incapable of entering into combination with other bodies of known molecular weight, the results of " substitution " afford information in the direction required. To take an instance, the hydrocarbon benzene is a neutral liquid, neither acid nor basic, which forms no compounds whose constitution throws any light on the question of its molecular weight. It is volatile, and its vapour density would tell all that we require to know ; namely, that to represent a molecule of it, we must use the formula C_6H_6 ; but even if we had not this evidence to appeal to, the same result would be indicated by the com- position of the products which are formed from it under the agency of chlorine.   Acted upon in this way, benzene yields the following series of compounds :—

$$C_6H_6$$
$$C_6H_5Cl$$
$$C_6H_4Cl_2$$
$$C_6H_3Cl_3$$
$$C_6H_2Cl_4$$
$$C_6HCl_5$$
$$C_6Cl_6$$
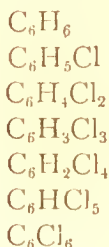
From these formulæ, it is clear that the operation con- sists in the removal of successive atoms of hydrogen, and

* There are some exceptions, *e.g.*, polyamines, which cannot be dis- cussed here.

their replacement by atoms of chlorine ; and consequently that a molecule of benzene is formed of six atoms of carbon associated with six atoms of hydrogen. This is a method of investigation very frequently resorted to among carbon compounds, and one of which examples will readily occur to the student.

But notwithstanding the multiplicity of the rules which serve to guide chemists in the selection of formulæ whereby to represent molecules, there still remain a large number of bodies which cannot be dealt with by any method at present known. Hence many of the formulæ commonly accepted and employed in chemical works are at best expressions of mere guesses enjoying various degrees of probability. Many difficulties occur, for example, among metallic compounds. The formula CrO_3 is generally used for chromic anhydride, not on account of any direct evidence in favour of it, but because of the existence of a volatile oxychloride CrO_2Cl_2, and the analogy of these two compounds with sulphuric anhydride, SO_3, and the corresponding oxychloride SO_2Cl_2, also on account of the isomorphism of the chromates and sulphates. Again, potassium permanganate is sometimes expressed by the formula $KMnO_4$, which recalls its isomorphism with the perchlorate $KClO_4$, but the double formula $K_2Mn_2O_8$ has something to recommend it as satisfying the law of even numbers.* So also doubts exist as to the correct mode of representing salts like ferrous and stannous chlorides, there being some probability that the usual formulæ $FeCl_2$ and $SnCl_2$ should be doubled in order to represent the reacting units or molecules of these compounds.

* See Chap. XIX.

K

CHAPTER XVII.

DISSOCIATION.

A LUMP of solid ammonium carbonate, or a solution of the same salt, exposed to atmospheric air at common temperatures, loses ammonia, which escapes together with the vapour of water, and the solution, originally alkaline, becomes after a time neutral. The change may be thus represented :

$$\cdot\ (NH_3)_2.OH_2.CO_2\ =\ NH_3.OH_2CO_2\ +\ NH_3$$

Ammonium Carbonate.   Ammonium Bicarbonate.
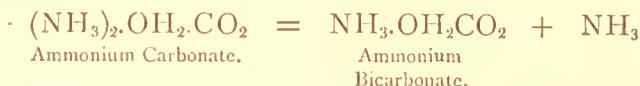
Or when a solution of ammonium oxalate, chloride or nitrate is boiled, a similar escape of ammonia may be observed, and the liquid acquires a distinctly acid reaction.

$$(NH_3)_2H_2C_2O_4\ =\ NH_3H_2C_2O_4\ +\ NH_3$$

Ammonium oxalate.   Ammonium acid oxalate.
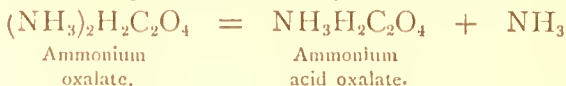
And if in either of these cases the ammonia thus evolved is brought into contact at a lower temperature with the solution from which it was produced, it will enter again into combination, and the original compound will be regenerated.

Again, when calcium carbonate is heated strongly in a vessel from which the air has been more or less completely removed by the air-pump, it suffers decomposition into lime which remains behind, and carbon dioxide gas which fills the vessel, $CaCO_3 = CaO + CO_2$, and this decomposition proceeds until the evolved gas acquires a certain density or tension, which increases as the temperature rises. If now the whole is allowed to cool, the carbonic acid gas slowly recombines with the lime, and a vacuum is once more established. Calcium carbonate splits up in the same manner when a current of steam, or other gas into which the carbonic anhydride can diffuse, is passed over it whilst under the action of heat.

Decompositions like that of the ammonium salts or of calcium carbonate under the influence of heat, are examples of what is known as *dissociation*, or, as it is sometimes more precisely termed, *thermolysis*. The word dissociation has acquired by careless use some degree of ambiguity, but in these pages its application will be restricted solely to those cases of decomposition in which certain bodies are resolved at an elevated temperature into simpler bodies, which are capable of reuniting and reproducing the original compound when the temperature is again allowed to fall.*

We shall now consider several cases of dissociation.

A crystal of sulphate of copper remains unaltered at ordinary temperatures in moist air ; but if moderately heated, it loses its water of crystallisation, and crumbles down to a white powder.

The same kind of decomposition takes place in many cases at the temperature of the air, and under ordinary conditions. Salts, which thus readily part with their water of crystallisation and fall away to powder, are said to be *efflorescent*. Sulphate, carbonate, and phosphate of sodium afford examples of this kind of dissociation, which, however, presents nothing remarkable beyond the fact of occurring at comparatively low temperatures. In this respect, however, these phenomena are surpassed by those exhibited by salts, which, under ordinary circumstances, are deposited from solution void of water of crystallisation. As already mentioned (Chapter II, p. 12), such compounds have been found in every instance to combine with water when crystallised at temperatures below zero. The explanation of the existence of anhydrous crystals is simply that dissociation of the salt from the water occurs at or below the temperature at which the crystals are deposited. And even those salts which usually combine with water of crystallisation may be obtained

* The decomposition of ferric salts and other similar compounds, when heated with water, ought not to be represented as cases of dissociation, being in reality the effects of mass. See Chap. XIII.

in a lower state of hydration, or altogether destitute of water by causing them to crystallise at more or less elevated temperatures. Sodium sulphate furnishes a case in point. The crystals of this salt formed at ordinary temperatures contain ten molecules of water of crystallisation combined with one of the salt ($Na_2 SO_4. 10OH_2$) ; when formed at $18°$ they contain seven molecules of water ($Na_2 SO_4.7OH_2$), whilst a solution heated to $34°$ yields crystals which contain no water at all. Similar phenomena are beautifully exhibited when the solutions of some coloured salts are heated. Chloride of cobalt especially lends itself to this kind of reaction. This salt forms crystals consisting of $CoCl_2 + 6OH_2$, and when dissolved in water it gives a red solution ; but if the temperature is raised even very slightly the liquid changes in colour, becoming successively purple and blue, and these changes correspond with the formation of the compounds $CoCl_2 + 4OH_2$ and $CoCl_2 + 2OH_2$ respectively. When the temperature is again allowed to fall, the solution reassumes its original red colour. This sort of dissociation, however, is not confined to water presumably subsisting as such in crystallised salts. Cases are by no means unknown in which a more profound decomposition is effected by the same agency of heat.

Thus, sulphuric acid of any strength, whether containing excess of water or excess of sulphuric anhydride, when evaporated till a liquid of constant composition is obtained, leaves, not pure hydrogen sulphate, H_2SO_4, but a mixture containing the elements of that body with about $1\frac{1}{2}$ per cent. of water. And if pure hydrogen sulphate is heated to between $30°$ and $40°$, it gives off vapours of SO_3, so as gradually to become reduced to the condition of common oil of vitriol, the stable hydrate referred to above.

Furthermore, it is found that the specific gravity of the vapour of this compound is only about one quarter and not one half of the molecular weight as represented by the formula H_2SO_4, that is instead of being, in accordance

with the general rule (Chap. XVI, p. 121), 49 times as heavy as an equal volume of hydrogen taken at the same temperature, it is only $\frac{49}{2} = 24\frac{1}{2}$ times as heavy, or thereabouts.

The physical explanation of these phenomena is to be found in a theory which has been already partly discussed (Chap. XIII.). We have every reason to believe that the phenomena observed are the results of two opposite and reciprocal actions : the one of decomposition, the other of recombination proceeding simultaneously. At low temperatures, when the composition of hydric sulphate is accurately represented by the formula H_2SO_4 or H_2O, SO_3, the number of molecules decomposed into H_2O and SO_3 is exactly counterbalanced by the number of molecules which are reconstituted in the same period by the reunion of these two substances. As the temperature rises and the agitation of the molecules in the mass becomes more vigorous, the number of molecules which undergo decomposition progressively increases, whilst the recombination *pari passu* continually decreases, till at length a point is reached in which the SO_3 molecules, and the OH_2 molecules become indifferent to each other, and recombination no longer takes place. When the temperature is allowed to fall these processes are reversed, and for every degree of temperature a certain definite relation subsists between the decomposition and recomposition, so that a kind of equilibrium is maintained. The compensating process being at high temperatures annulled, decomposition is complete, the vapour consists throughout of a uniform mixture of two different kinds of molecules, and consequently, by the law of Avogadro, it occupies twice the volume it would otherwise fill if dissociation did not take place. The chemically reacting unit of sulphuric acid H_2SO_4 is apparently incapable of subsisting in the state of vapour, and thus no conclusion respecting the chemical molecule of this body can be drawn from the specific gravity of its vapour.

Ammonium chloride furnishes another instance in which

the usual relation between the vapour density and molecular weight is not preserved. The specific gravity of the vapour of ammonium chloride is only about $13\frac{1}{2}$ instead of 27 as we should expect it to be. This anomaly is explained by the assumption that the vapour evolved by ammonium chloride is in reality formed of a mixture of ammonia and hydrochloric acid, which occupy double the volume they would fill if bound up together in a single molecule undivided by heat.

In like manner, under ordinary circumstances, phosphoric chloride dissociates into phosphorous chloride and free chlorine, and calomel in vapour becomes a mixture of mercuric chloride and mercury.

That the vapour densities of all these compounds are less than they should be according to theory, or, in other words, the vapour-volumes of their molecules are greater than the volume occupied by all other vaporisable molecules, is a fact which cannot be disputed. That these anomalies may be ascribed to dissociation is also admitted on all hands, but the direct proof that dissociation has taken place in a given vapour is by no means easy to supply.

In the case of sulphuric acid and of ammonium chloride, advantage has been taken of the difference in the diffusibility of the products into which these bodies are supposed to dissociate. Thus the vapour of sulphuric anhydride is much heavier and consequently less diffusible than vapour of water, so that when sulphuric acid is heated for several hours in a vessel with a capillary orifice, the water vapour escapes more rapidly than the sulphuric anhydride, and the latter gradually accumulates in the residue. Pentachloride of phosphorus has also been resolved into free chlorine and phosphorus trichloride, which may be to some extent separated by diffusion. Phosphorus pentachloride has been found to possess a normal vapour density when mixed with a sufficient quantity of the trichloride to prevent dissociation.

In the case of sublimed calomel, we are enabled to con-

vict this substance of having submitted to dissociation whilst in the state of vapour, by appealing to the fact, well known to manufacturers, that it invariably contains small quantities of corrosive sublimate, and sometimes of metallic mercury, which have escaped recombination during the cooling down of the vapour.

The following is a list of the most important cases of vaporous dissociation :—

Nature of decomposition of dissociated Molecule.			Vapour Volume.
Phosphoric chloride. PCl_5 =	Phosphorous chloride. PCl_3 +	Chlorine. Cl_2	vols. 4
Nitric oxide. N_2O_2	(See Chapter XIX.)		4
Nitric peroxide. N_2O_4 =	NO_2 + (See Chapter XIX.)	NO_2	4
Chloric peroxide. Cl_2O_4			3?
Sulphuric acid. H_2SO_4 =	Water. H_2O +	Sulphur trioxide. SO_3	4
Ammonium chloride. NH_4Cl =	Ammonia. NH_3 +	Hydrochloric acid. HCl	4
Ammonium sulphydrate. NH_4HS =	Ammonia. NH_3 +	Hydrogen sulphide. H_2S	4
Isoamylic iodide. $C_5H_{11}I$ =	Amylene. $C_5H_1{}^0$ +	Hydriodic acid. HI	4

CHAPTER XVIII.

TYPES.—ATOMICITY.

BODIES which are capable of entering into chemical reactions in the same manner, giving rise under similar circumstances to new products, having similar properties, are said to belong to the same type. The idea that the chemical constitution of all known bodies is modelled

upon a certain limited number of types supplies a means of classifying them according to their modes of transformation. Thus water is capable, in a variety of ways, of exchanging its oxygen and hydrogen for other elements and groups of elements (compound radicles), and the bodies which result from these exchanges retain, more or less perfectly, the chemical deportment of water, and are said to belong to the water type. Caustic potash, for example, is referred to the water type because, like water, it is capable of exchanging its oxygen for sulphur, and its hydrogen for a metal, for an elementary atom like chlorine, or for a group of atoms, such as ethyl or acetyl. As a memorandum of the correspondence in these transformations, the two series of derivatives may be formulated in a similar manner. Thus :

$$\left.\begin{matrix} H \\ H \end{matrix}\right\}O \qquad\qquad \left.\begin{matrix} K \\ H \end{matrix}\right\}O$$

$$\left.\begin{matrix} H \\ H \end{matrix}\right\}S \qquad\qquad \left.\begin{matrix} K \\ H \end{matrix}\right\}S$$

$$\left.\begin{matrix} H \\ Cl \end{matrix}\right\}O \qquad\qquad \left.\begin{matrix} K \\ Cl \end{matrix}\right\}O$$

$$\left.\begin{matrix} H \\ C_2H_5 \end{matrix}\right\}O \qquad\qquad \left.\begin{matrix} K \\ C_2H_5 \end{matrix}\right\}O$$

$$\left.\begin{matrix} H \\ C_2H_3O \end{matrix}\right\}O \qquad\qquad \left.\begin{matrix} K \\ C_2H_3O \end{matrix}\right\}O$$

&c. &c.
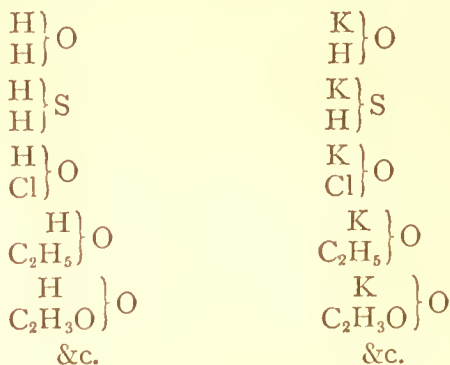
Formulæ of this kind are often spoken of as *rational* formulæ. But water is not the only type. Hydrogen, hydrochloric acid, ammonia, and marsh-gas are other bodies which are often referred to as types of decomposition, each of which is imitated, more or less closely, by a considerable number of elements and compounds. The student will readily perceive that the list of bodies which might, for special purposes, be selected as types, may be extended and varied almost indefinitely.

This plan of registering in the formula some of the facts

which have been observed as to the possible transforma-
tions of a body, has led some chemists to infer that it is
possible to represent symbolically the relative positions
occupied by the atoms contained in molecules. The
student will do well to approach such an idea with caution.
Rational or descriptive formulæ of various kinds are
valuable not only as memoranda of the possible modes of
formation and decomposition of bodies, but are positively
necessary to enable us to distinguish from one another
bodies having the same ultimate composition, but different
properties. But we know very little regarding the essential
nature of molecules, and still less of their constituent
atoms ; and it is, to say the least, premature to attribute to
these formulæ a meaning which has so little to support it.

Sulphuric acid furnishes a very good example of the kind of
fact and argument upon which rational formulæ are based.
In this case, mere analysis tells us only that the compound
contains an atom of sulphur, two atoms of hydrogen, and
four atoms of oxygen, or SH_2O_4. But on examination of its
salts, we find that both the atoms of hydrogen are replace-
able by metals ; and to indicate this basic function of the
hydrogen, it is the custom to write it at the beginning of
the formula, thus,

$$H_2SO_4.$$

When sulphuric acid is distilled with phosphoric chloride,
it yields two products having respectively the formulæ

$$SO_3HCl \qquad \text{and} \qquad SO_2Cl_2.$$
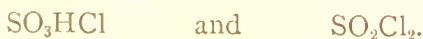
The former of these bodies results from the removal of an
atom of oxygen and an atom of hydrogen from the sulphuric
acid, whilst an atom of chlorine is taken up.

$$SO_4H_2 - OH + Cl = SO_3HCl.$$

And this exchange is repeated when the second derivative
is produced.

$$SO_3HCl - OH + Cl = SO_2Cl_2.$$
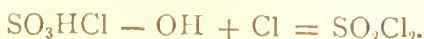
Either of the new compounds will reproduce sulphuric
с id when dissolved in water. It seems, therefore, that
sulphuric acid is capable of breaking up into the groups
SO_2 and $2HO$. And this is confirmed by the fact of the
production of sulphates by the union of sulphur dioxide
with peroxides, as in these instances :—

$$PbO_2 \quad + \quad SO_2 \quad = \quad PbO_2SO_2$$
Lead peroxide.   Sulphur dioxide.   Lead sulphate.

$$(HO)_2 \quad + \quad SO_2 \quad = \quad (HO)_2SO_2$$
Hydrogen   Sulphur   Hydrogen sulphate,
peroxide.   dioxide.   or sulphuric acid.
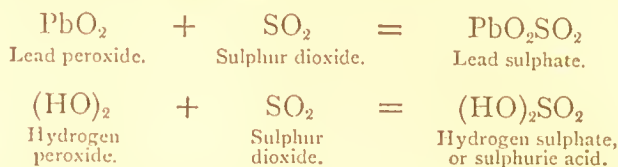
Such reactions as these and many others are recalled
when we write the formula

$$\left.\begin{array}{l} HO \\ HO \end{array}\right\} SO_2$$

or,

$$\begin{array}{l} H \\ SO_2 \\ H \end{array} \left.\begin{array}{l} \\ \end{array}\right\} O \; \left.\right\} O$$
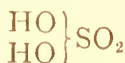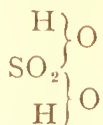
in which it may be regarded as a derivative from two
molecules of water, each of which has lost an atom of
hydrogen, so that the two residues are united together by
the group SO_2.

But there are many cases in which we write such descrip-
tive formulæ with the utmost confidence that they express
possible reactions, although such reactions, for various
reasons, may never have been observed.

The formulæ that we now make use of are, to a great
extent, based upon certain assumptions regarding those
chemical properties of atoms which are referred to under
the name " atomicity."

In the formulæ

$$ClH \qquad OH_2 \qquad NH_3 \qquad CH_4$$
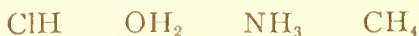
we see one atom of chlorine combined with one atom of

hydrogen ; one atom of oxygen with two of hydrogen ; one atom of nitrogen with three of hydrogen ; and one atom of carbon with four atoms of hydrogen ; and no compound is known in which one atom of either of these elements— chlorine, oxygen, nitrogen, or carbon—is united with a larger quantity of hydrogen than is represented here.

This difference of combining capacity is further illustrated by the fact that when chlorine is made to act upon water, ammonia, or marsh-gas, the hydrogen contained in one molecule of each of these compounds is distributed into so many separate molecules of hydrochloric acid. Thus,

2 volumes of water vapour.
OH_2

$+$

2 volumes of chlorine.
Cl

give

1 volume of oxygen.
O

$+$

4 volumes of hydrochloric acid.
$2HCl$

Again,

$$NH_3 \quad + \quad 3Cl \quad = \quad 3HCl \quad + \quad N$$
2 Volumes.   3 Volumes.   6 Volumes.   1 Volume.

The following succession of changes indicates the same thing in the case of marsh-gas :—

1. $CH_4 \quad + \quad Cl_2 \quad = \quad CH_3Cl \quad + \quad HCl$
    2 Volumes.   2 Volumes.   2 Volumes.   2 Volumes.

2. $CH_3Cl \quad + \quad Cl_2 \quad = \quad CH_2Cl_2 \quad + \quad HCl$

3. $CH_2Cl_2 \quad + \quad Cl_2 \quad = \quad CHCl_3 \quad + \quad HCl$

4. $CHCl_3 \quad + \quad Cl_2 \quad = \quad CCl_4 \quad + \quad HCl$

Thus the four atoms of hydrogen which, by the carbon in the marsh-gas, were united together into one molecule,

measuring 2 volumes, are separated into four molecules or
eight volumes of hydrochloric acid.

| H | Cl |

| C | H⁴ | yields

| H | Cl |

| H | Cl |

| H | Cl |

| H | Cl |
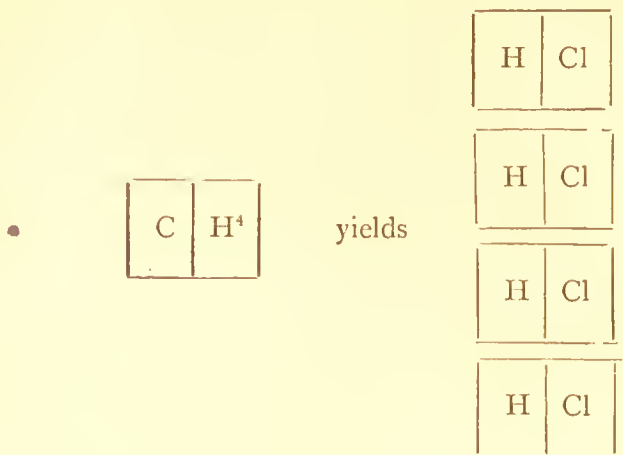
In these cases, therefore, the combining value of an atom
of chlorine is equal to that of one atom of hydrogen ; it is
univalent. We summarise these relations when we say that
chlorine is a *monad*, because we never find it linked to more
than one atom at a time. Hydrogen must also be a monad,
for in the production of the compound HCl, whatever is the
attraction of the chlorine for the hydrogen, there must be an
equal attraction on the part of the hydrogen for the chlorine.

As the result of similar observations, we find that the
atom of oxygen is diad, of nitrogen triad or pentad, of
carbon tetrad, the combining capacity or " valency " being
in each case measured by the number of univalent atoms,
such as hydrogen or chlorine, which one atom of these
elements can respectively combine with or replace.

The valency of the elementary atoms, though varying, is
limited, and in different cases attains a different maximum.
The term " atomicity " is employed to indicate the greatest
number of atoms of one kind or another with which a given
atom is ever observed to be united. To what the variation
of valency may be due it is impossible to say in the present

state of knowledge ; it seems, at any rate, to have no very obvious relation either to the atomic weight or to the chemical energy of the element.*

The atomicity of a few of the rare elements is still in obscurity, in consequence either of doubts regarding their atomic weights or a want of knowledge as to the composition of their compounds ; but those which have been sufficiently studied admit of classification into the six divisions displayed in the following table :—

ATOMICITY OF THE PRINCIPAL ELEMENTS.

NON-METALS.					
Monads.	Diads.	Triads.	Tetrads.	Pentads.	Hexads.
F	O	B	C	N	S
Cl			Si	P	Se
Br					Te
I					

METALS AND METALLOIDS.					
Ag	Hg	Au	Ir Ro	V	Os Ru
	Cu	In	Pt Pd	As	W
H	Cd	Tl		Sb	Mo
Li	Zn		Pb	Bi	U
Na	Mg		Sn		Cr
K	Ca		Ti	Ta	Mn
Rb	Sr		Zr	Nb	Fe
Cs	Ba		Al		
			Co		
			Ni		

* Many facts seem to point to the conclusion that there is no absolute measure of atomicity. The capacity of saturation of a given atom depends upon the nature of the elements with which it is associated.

An arrangement of this kind necessarily involves the separation of many elements which, in properties, are closely allied together, and the association of others which have very little in common. Thus we have to look for thallium among the triads, although it has strong points of resemblance on the one hand to the alkali metals, and on the other hand to lead. Oxygen, again, is separated from sulphur, aluminium from chromium and iron, lead from barium. This part of the subject will be again adverted to in a later chapter.

Any portion of a molecule which is capable of being detached and transferred to some other molecule by way of decomposition is called a " radicle," whether it consist of a single atom or of a group of atoms. The term " compound radicle " is, however, not usually applied to a group unless it makes its appearance in several different bodies. Compound radicles present different degrees of quantivalence, just as do the atoms of which they are built up, so that they are capable of linking together various proportions of other elementary or compound radicles. This fact may be experimentally verified by such reactions as the following :—

Ordinary disodic phosphate is alkaline to test-paper, silver nitrate is neutral. When these two salts are mixed

An atom of sulphur can take up no more than two atoms of hydrogen, but it is capable of forming a compound with four atoms of chlorine, or with three atoms of oxygen. In like manner, phosphorus forms the compounds PCl_3 and PCl_5, but its affinity for hydrogen extends only to three atoms, PH_3, though a fourth may be taken up if accompanied by an atom of iodine — PH_4I. It has also been observed that the chlorides corresponding with the highest oxides of many of the metals have not yet been produced, and seem to be incapable of existing. Thus there are the oxides CrO_3, UO_3, As_2O_5, Ni_2O_3, but the chlorides Cr_2Cl_6, UCl_5, $AsCl_3$, and $NiCl_2$ indicate the limits of the capacity of these metals for chlorine. It is interesting to notice that in some cases in which the chloride is missing, the corresponding fluoride is known. The fluorides CrF_6 and AsF_5, the representatives of the unknown chlorides $CrCl_6$ and $AsCl_5$, have been described.

together in equivalent proportions a yellow precipitate of phosphate of silver is thrown down, whilst the liquid becomes strongly acid. The reason of this is apparent when we express the metathesis in the form of an equation.

$$\left.\begin{matrix} Na \\ Na \\ H \end{matrix}\right\} PO_4 \quad + \quad \left.\begin{matrix} AgNO_3 \\ AgNO_3 \\ AgNO_3 \end{matrix}\right| \quad = \quad \left.\begin{matrix} Ag \\ Ag \\ Ag \end{matrix}\right\} PO^4 \quad + \quad \left.\begin{matrix} NaNO_3 \\ NaNO_3 \end{matrix}\right|$$

One molecule. Three molecules. One molecule Two molecules of
                                 of silver phosphate. sodium nitrate.

$$+ \quad \boxed{HNO_3}$$

One molecule
of nitric acid.
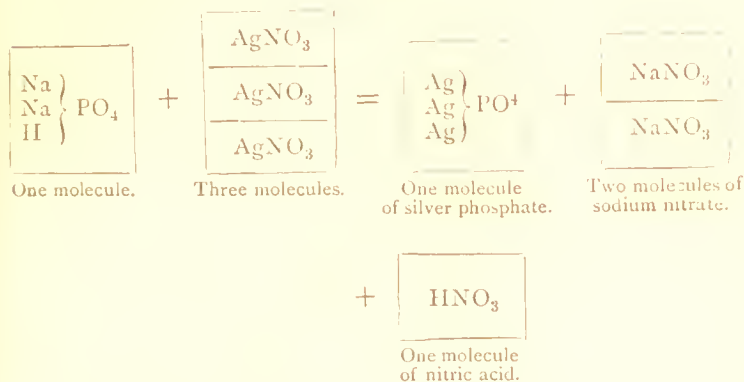
The group PO_4 is trivalent, and so it holds together the two atoms of sodium and one atom of hydrogen in one molecule. But when the interchange occurs, these become respectively united with three (NO_3) groups, each of which is univalent, and incapable of connecting itself with more than one atom at a time. Three new molecules result, one of which is nitric acid, the presence of which can be recognised by test papers.

The compound resulting from the union of two or more atoms is called a saturated compound, when the atomicity of each atom present is satisfied. This condition is fulfilled when one atom of a monad is combined with another monad, or when two atoms of a monad combine with one atom of a diad, or three of a monad with one of a triad, four monad or two diad atoms with one tetrad, and so forth.

Examples of various orders of compounds are shown in the following formulæ, in which the combining power of each atom present is supposed to be neutralised by that of

other atoms. In the notation here introduced, it must be understood that the symbol placed on the left of a formula represents an atom to which all on the same line are directly united. Those also which are connected by a bracket, are united together. Thus,

$$\begin{cases} CH_3 \\ CH_3 \end{cases}$$

means that there are two atoms of tetrad carbon united by one-fourth of their combining power, whilst each retains three atoms of hydrogen. The same relations are expressed in this figure, or " graphic formula."

$$
\begin{array}{ccc}
H & & H \\
| & & | \\
H-C & - & C-H \\
| & & | \\
H & & H
\end{array}
$$
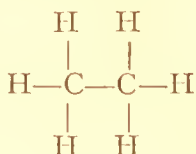
Of course the lines connecting the symbols are not designed to represent any substantive bond or link, but merely indicate the manner in which the combining capacity of each atom is disposed of.

EXAMPLES OF CONSTITUTIONAL AND GRAPHIC FORMULÆ.

Hydrochloric acid.
    HCl   or   H—Cl

Water.
    OH_2 or   H—O—H

Copper sulphide.
    CuS   or   Cu—S

Hydrogen peroxide.
    $\begin{cases} OH \\ OH \end{cases}$ or   H—O—O—H

Phosphoric chloride.
    PCl_5 or
$$
\begin{array}{c}
Cl \\
| \\
Cl-P-Cl \\
\diagup \diagdown \\
Cl \quad Cl
\end{array}
$$

Stannic chloride.
$SnCl_4$ or

$$Cl-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{Sn}}-Cl$$

Phosphoric oxide.
$\begin{cases} PO_2 \\ O \\ PO_2 \end{cases}$ or

$$\overset{O}{\underset{O}{\overset{\|}{P}}} - O - \overset{O}{\underset{O}{\overset{\|}{P}}}$$

Acetic acid.
$\begin{cases} CH_3 \\ CO(OH) \end{cases}$

$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

Aluminic chloride.
$\begin{cases} AlCl_3 \\ AlCl_3 \end{cases}$ or

$$Cl-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{Al}}-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{Al}}-Cl$$

Sulphuric acid
$SO_2(OH)_2$ or

$$\begin{matrix} H-O \\ \\ H-O \end{matrix} \diagdown S \diagup \begin{matrix} O \\ \\ O \end{matrix}$$

Potassium dichromate.
$\begin{cases} CrO_2(OK) \\ O \\ CrO_2(OK) \end{cases}$ or $K-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-O-K$

L
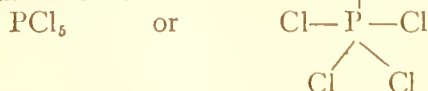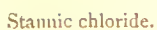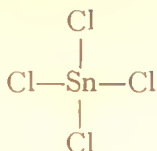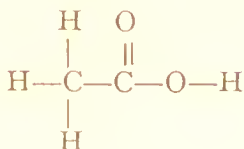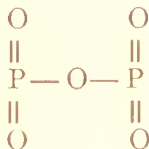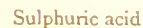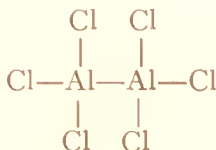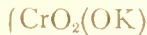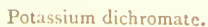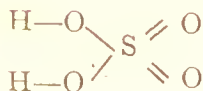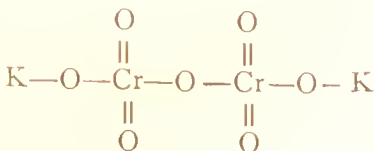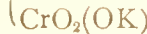
CHAPTER XIX.

UNSATURATED COMPOUNDS.

WHEN several compounds are formed by the union of two elements in different proportions, it is very commonly noticed that the change of valency or combining capacity of the central atom to which the rest may be supposed to be attached, takes place by pairs of units.

Thallium, tin, and phosphorus, for example, each form two chlorides ; nitrogen combines with three atoms of hydrogen in ammonia, and with four atoms of hydrogen and an atom of chlorine in chloride of ammonium. Sulphur also yields compounds, in which one atom of that element is combined with two atoms of hydrogen, with two atoms of oxygen, and with two atoms of oxygen and two atoms of chlorine. The formulæ of these compounds are represented as follows :—

$$TlCl \quad SnCl_2 \quad PCl_3 \quad NH_3 \quad SH_2$$
$$TlCl_3 \quad SnCl_4 \quad PCl_5 \quad NH_4Cl \quad SO_2$$
$$S \begin{cases} O_2 \\ Cl_2 \end{cases}$$
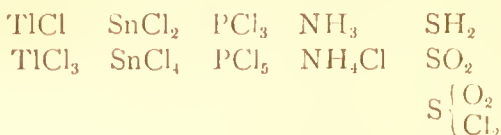
It will be observed that the difference in the first three cases amounts to two atoms of chlorine, which represent two atoms of hydrogen, the unit of valency. In the fourth case, one atom of hydrogen and one atom of chlorine have been added. In the fifth, the oxide SO_2 may be taken to represent a hypothetical hydride SH_4, whilst the oxychloride corresponds with the unknown compound SH_6. In each series, the advance in combining power is equivalent to the assumption of two atoms of hydrogen. And so it is in a large number of other cases.

It seems, therefore, that, as a general rule, the index of valency of any given atom is either an even or an odd number ; or, as it has been expressed, elements are

uniformly either " artiad " or " perissad." * So that in all
saturated compounds, and in the great majority of unsatu-
rated compounds, the sum of the indices of valency of all
the atoms present is an even number.

But there are not wanting exceptions to these statements ;
and although the number is at present not great, the marked
characters of these exceptions is sufficient to destroy much
of the apparent significance of those more numerous in-
stances which conform with them.

The following are some of the most notable instances :—

Nitric Oxide.— This most remarkable compound is a
colourless unliquefiable gas, almost insoluble in water, and
unchanged by heat. It exhibits all the characteristics of
an unsaturated compound. Thus it unites with oxygen,
with chlorine, with sulphuric anhydride, and with many
metallic salts.

It is composed of 14 parts of nitrogen with 16 parts of oxy-
gen ; its specific gravity is 15 ($H = 1$), and consequently
its molecular weight is 30. It therefore contains one atom
of nitrogen (perissad), combined with one atom of oxygen
(artiad), and thus it breaks the law of even numbers. This
difficulty might be avoided by employing the double formula,

$$N_2O_2 \text{ or } N = O$$
$$|||$$
$$N = O$$

but that its specific gravity and incondensability point con-
clusively to the simpler expression NO as the symbol of its
molecule.

Nitric Peroxide.—Below 9° this compound seems to be
a colourless liquid, which solidifies at very low tempera-
tures. But it cannot be volatilised without more or less
complete dissociation. At the lowest temperature, 4°·2, at
which its vapour has been examined, the vapour density
was found to be 2·588 (air $= 1$), whilst the formula N_2O_4
requires the vapour density to be 3·1786.

* ἄρτιος even, and περισσός odd.

When the temperature of the vapour is gradually raised its orange colour deepens, till at about 180° it becomes almost black, and the density is then 1·589. In this condition the formula NO_2 represents two volumes of the gas. This difference of constitution at high and low temperatures is further indicated by the fact that nitric peroxide does not combine with chlorine in the cold, although it does so when heated.

Uranium Pentachloride. (UCl_5 Roscoe).—This compound has recently been described, but as it cannot be converted into vapour without decomposition, its molecular weight is unknown. It is not improbable, therefore, that the molecule of the solid may really be

$$U_2Cl_{10} \quad or \quad UCl_5$$
$$|$$
$$UCl_5$$
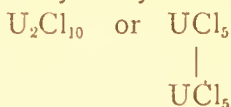
in which case it would present nothing unusual from the point of view now under consideration.

Tungsten and Molybdenum Pentachlorides, WCl_5 and $MoCl_5$.—These compounds afford very remarkable instances of the association of an artiad atom with an uneven number of perissad atoms, and consequent infraction of the law under discussion. Hexachlorides of both these elements, corresponding with their trioxides, exist ; but these chlorides when heated are split up into pentachlorides and free chlorine. The pentachlorides are volatile without decomposition, and tne vapours exhibit normal densities.

Although nearly all unsaturated compounds are capable of entering into combination, and many of them perform the part of well-defined radicles, it does not follow that all radicles should be capable of isolation, and the definition of a radicle (p. 142) by no means involves this idea. On the contrary, we have already examined phenomena (pp. 124, 125) which indicate that when a radicle of uneven quantivalence, such as H, Cl or N is liberated from combination, its atoms combine in pairs, and thus satisfy each other's attractions,

unless they find themselves in the presence of other radicles with which they can immediately unite. Compound radicles resemble elementary atoms in this respect. None of the following groups, for example, are known in the free state, the formulæ* representing semimolecules, or what may be termed chemical atoms of these radicles.

Hydroxyl (OH)′ contained in acids, alcohols, and metallic hydrates.
Potassoxyl (OK)′ contained in potassium oxysalts.
Cyanogen (CN)′ contained in cyanides.
Ammonium (NH$_4$)′ contained in the salts of ammonia.
Arsendimethyl $\left(As\frac{CH_3}{CH_3}\right)'$ in kakodyl and its compounds.
Methyl (CH$_3$)′ in methylic alcohol and derivatives.
Amidogen (NH$_2$)′ in primary amines and amides.
Methenyl (CH)‴ in chloroform and similar bodies.

When displaced from any of their compounds they do not remain isolated, but unite in pairs, producing molecules which in some cases are stable enough to maintain an independent existence.

We have for example,

Radicle Name.		Corporate Name.	
Hydroxyl	.	Hydric Peroxide	(OH)$_2$ or O$_2$H$_2$
Potassoxyl	.	Potassic Dioxide	(OK)$_2$ or O$_2$K$_2$
Cyanogen	.	Cyanogen Gas	(CN)$_2$ or C$_2$N$_2$
Arsendimethyl	Kakodyl		$\left(As\frac{CH_3}{CH_3}\right)_2$ or As$_2$(CH$_3$)$_4$
Methyl	.	Ethane	(CH$_3$)$_2$ or C$_2$H$_6$.
Methenyl	.	Acetylene	(CH)$_2$ or C$_2$H$_2$.

The only free monad radicles known are the two bodies already described, namely, nitrosyl, or nitric oxide, NO, and nitryl or nitric peroxide, NO$_2$. Instances of free diad radicles are, however, more numerous. Thus we have,

* The dashes serve to indicate the usual valency of each group.

Mercury	.	.	.	Hg''
Cadmium	.	.	.	Cd''
Carbonic oxide (carbonyl)		.	$(CO)''$
Sulphur dioxide (theionyl)		.	$(SO_2)''$
Ethene	.	.	.	$(C_2H_4)''$
Ammonia	.	.	.	$(NH_2)''$

Molecules of this kind are of the same order as those referred to at the beginning of the chapter, but why in so many cases the number of unemployed units of valency should be an even number, has not yet been satisfactorily explained.

An element in a free or unsaturated state may be compared to a body which has been raised to a height. In order to lift a body into an elevated position energy in some form must be expended, but the whole of that energy is recoverable in the form of heat or mechanical force when the body descends to its former level. It is just the same with a chemical element. Mechanical force, or its equivalent in the form of heat or electricity, is consumed when a chemical compound is resolved into its constituents, and when these constituents come together again the same amount of energy is called into action.

A body in an unsaturated state, then, like a stone on the roof of a house, possesses a store of potential energy which may at any time be called into activity.

Accepting the definition of a "radicle" given in the last chapter, it is obvious that there are a great many commonly recognized radicles which can hardly be expected ever to assume a bodily existence apart from the compounds in which they occur associated with elements of a different chemical character.

In all the carbonates, for example, a group consisting of one atom of carbon and three atoms of oxygen occurs, and this group is capable of being exchanged for Cl_2 or $(OH)_2$ or O by double decomposition. It is, therefore, entitled

to be spoken of as a compound radicle, although, by reason of the large proportion of oxygen it contains, its condition would be that of unstable equilibrium, even if it could assume temporarily an isolated existence.

Similar remarks apply to such radicles as NO_3 (of nitrates), ClO_3 (of chlorates), SO_4 (of sulphates), PO_4 (of phosphates), and the rest, which under possible experimental conditions, have never yet been isolated.

But, after all, it is necessary to remind the student that our system of notation is to be understood and employed only in a unitary sense. Every molecule is, with reason, regarded as one entire and undivided unit, whose actions and reactions proceed, not from the affinities of this or that element contained within it, but from the resultant of all the different forces, exerted by its several constituent parts.

A chemical compound may be compared to a musical chord, constituted, doubtless, of many and complex elements, but communicating to the ear the impression of singleness and harmony.

The doctrine of radicles, no less than that of atomicity, and the graphic notation founded upon it, is at present to be regarded solely in the light of a convenient, but not absolutely necessary, system of recording and comparing facts concerning the changes of composition to which bodies are subject under the influence of chemical attraction.

Note.—The following memoranda will serve to assist the student in writing the formulæ of many common salts. In order to construct any required formula it is only necessary to place a symbol or group of symbols, taken from under the positive sign, side by side with a symbol or group taken from under the negative sign, and to adjust the quantity of each so as to comply with their respective habits of combination.

Thus let
    R′ represent a univalent radicle,
    R″   ,,   ,, bivalent radicle,
    R‴   ,,   ,, trivalent radicle, etc.

Then it is only necessary to remember that

R′ combines with R′,
2 R′   ,,   ,,   R″,
or R″   ,,   ,,   R″,
3 R′   ,,   ,,   R‴,
3 R″   ,,   ,, 2 R‴, etc.

In this way the student will readily learn to compose the unitary formulæ of all the most commonly occurring compounds, without risk of falling into any serious error.

VALENCY OF COMMON SALT RADICLES.

Univalent −	Univalent +	Bivalent −	Bivalent +	Trivalent −	Trivalent +	Quadrivalent −	Quadrivalent +	Sexivalent +
F	H	O	Ba	PO_4 (ortho)	As	SiO_4 (ortho)	Sn (ic)	Al_2
Cl	K	S	Sr	AsO_3	Sb	P_2O^7 (pyro)	Pt	Cr_2 (ic)
Br	Na	SO_3	Ca	AsO_4	Bi			Fe_2 (ic)
I	NH_4	SO_4	Mg	BO_3	Au			Mn_2 (ic)
CN	Ag	S_2O_3	Zn					
HO		CO_3	Cd					
NO_2		C_2O_4	Hg (ic)					
NO_3		$C_4H_4O_6$	Cu (ic)					
ClO		SiO_2 (meta)	Pb					
ClO_2		CrO_4	Fe (ous)					
ClO_3		MnO_4	Mn (ous)					
ClO_4		Mn_2O_8	Sn (ous)					
PO_3 (meta)			Hg_2 (ous)					
$_2H_3O_2$			Cu_2 (ous)					

CHAPTER XX.

ISOMERISM.

SEVERAL bodies, though differing more or less in properties, may have the same composition. In such cases they are said to be *isomeric*. The differences observed among isomeric bodies sometimes extend only to their physical characteristics, sometimes to their chemical properties.

Several cases require therefore to be considered.

PHYSICAL ISOMERIDES.

Sulphur, when crystallised from carbon disulphide, yields rhombic octahedra, the specific gravity of which is 2·07 ; whereas, if melted and allowed to cool, it crystallises in oblique rhombic prisms, having the specific gravity 1·98. The prismatic variety soon changes spontaneously into the octahedral, which is the stable form, at the same time evolving heat. Sulphur is said to be *dimorphous*, as it crystallises in two forms, and these two modifications are often spoken of as allotropic states of the element.

Many other examples might be cited of the same sub-stance assuming different crystalline forms, the change of structure being almost invariably attended by differences of specific gravity and solubility. One form is generally less stable than the other, and sooner or later, especially under the influence of change of temperature, is converted into the permanent variety.

When, as in these cases, two bodies chemically alike exhibit slight differences of physical characters—such as solubility, crystalline form, specific gravity, or action upon light—they may be regarded as one and the same sub-stance, though more or less disguised, and such bodies may be distinguished as *physically isomeric.*

Examples of physical isomerism are not difficult to find either among mineral or carbonaceous compounds. Thus

we have the two varieties of native calcium carbonate, arragonite and Iceland spar, as well as the curious instance of change of colour accompanying change of crystalline structure in the two modifications of mercuric iodide ; whilst among carbon compounds, the varieties of tartaric acid (described in Chapter XII., p. 74) may be referred to, beside many members of the numerous class of hydrocarbons called terpenes. These terpenes (formula $C_{10}H_{16}$) consti- tute the chief ingredients in the essential oils of turpentine, lemon, orange and bergamot, and others. They have the same composition, and under the influence of chemical agents yield similar compounds, but they differ in odour, boiling point, and rotating action on a ray of polarised light.

The difference in all these cases probably arises not from any difference in chemical composition or constitution, but from the various modes in which the molecules of the bodies are associated together ; such modification being connected with some peculiarity in the circumstances attending their formation.

That a change of molecular structure is accompanied by a corresponding change of physical characters, is proved by the well-known fact that when a piece of glass is strongly compressed, either by mechanical means or by suddenly cooling it from a high temperature, it acquires the power of polarising light in a manner which it loses when the pressure is relieved.

It has also been found that the rotatory power of solids, when in solution, varies with the nature of the liquid (itself optically inactive) in which they are dissolved. This is in all probability due to the formation of molecular combina- tions, of various degrees of complexity, between the liquid and the dissolved substance. (See Chap. II., p. 10)

POLYMERIDES.

Bodies containing the same elements united in the same proportion, but having different molecular weights, belong

to this class of isomerides. The following are some ex-
amples :—

Sulphur boils at 440°, and is converted into an orange-
coloured vapour, the density of which, when taken at about
500°, is three times as great as it should be theoretically ;
whilst at 1000° it is only 32 times as great as that of
hydrogen at the same temperature and pressure, thus con-
forming with the ordinary rule. There seem, therefore, to
be two varieties of the gaseous sulphur molecule, one of
which is polymeric with the other. They may be repre-
sented by the formulæ

$$S_2 \text{ and } S_6.$$

Ozone, the molecule of which has been shown by various
facts and arguments to have the formula O_3, or $\frac{3}{2}O_2$, may
also be regarded as polymeric with ordinary oxygen, O_2.

The two varieties of nitric peroxide NO_2 and N_2O_4 have
already been described (p. 147). The latter is polymeric
with the former.

Of carbon compounds exhibiting similar relations, the hy-
drocarbons of the C_nH_{2n}, or olefine series, afford a prominent
instance. The formulæ of these bodies are all multiples of
the first, methene CH_2, which, however, is not known in
the free state. Being at once polymeric and homologous
with one another, they exhibit a regular gradation in their
boiling-points and specific gravities, and form similar che-
mical compounds.

Name.	Formula.	Boiling Point.
Ethene or ethylene .	C_2H_4	Gas, liquefiable only under great pressure.
Propene or propylene .	C_3H_6	—17·8
Quartene or butylene .	C_4H_8	3°
Quintene or amylene .	C_5H_{10}	35
Sextene or hexylene .	C_6H_{12}	68—70
etc.	etc.	etc.

Further illustrations are supplied by the two chlorides of cyanogen $CNCl$ and $C_3N_3Cl_3$; by cyanic acid $CNOH$ and cyanuric acid $C_3N_3O_3H_3$; also by the modifications of aldehyd C_2H_4O, acraldehyd $(C_2H_4O)_2$ or $C_4H_8O_2$, and paraldehyd $(C_2H_4O)_3$ or $C_6H_{12}O_3$, and many others.

METAMERIDES.

We have now to consider a kind of isomerism, which occurs very frequently among carbon compounds. The nature of the phenomenon will be understood by comparing together several such compounds as the following, all of which are represented by the same empirical formula :—

1. Propionic acid, $C_3H_6O_2$, is a crystallisable acid, which, after melting, boils at 140°. It is monobasic, forming one salt only with each of the metals, sodium, potassium, and silver. Its rational formula may, therefore, be written thus : $HC_3H_5O_2$.

2. Ethylic formate is a colourless aromatic liquid, which boils at 56°. When heated with caustic potash, it is resolved into ethylic alcohol and potassium formate. This mode of decomposition is recorded when we write the formula thus : $C_2H_5.CHO_2$.

3. Methylic acetate is a colourless, volatile liquid, which also boils at 56°, but when decomposed by an alkali, it yields wood spirit (methylic alcohol) and an acetate. So its formula must be $CH_3.C_2H_3O_2$.

These three compounds, which have the same composition and molecular weight, but differ in the nature of the products they yield, when decomposed or acted upon by chemical agents, are said to be *metameric* with one another.

Many cases similar to the last two may easily be found amongst ethereal salts (compound ethers), ketones and other bodies, the molecules of which consist of two compound radicles united together by oxygen or a bivalent group. Pairs of such bodies may be called reciprocal metamerides, because the excess of carbon and hydrogen in one of the

radicles is made up for by a corresponding deficiency in the other. General formulæ for such pairs of isomerides among the compound ethers might be written thus :

$$\left. \begin{array}{l} C_nH_{2n} - {_1}O \\ C_pH_{2p\,+\,1} \end{array} \right\}O \quad \text{and} \quad \left. \begin{array}{l} C_pH_{2p} - {_1}O \\ C_nH_{2n\,+\,1} \end{array} \right\}O$$

In many cases an extraordinary resemblance in physical properties may be observed in comparing together two bodies of this kind.

Another instructive example of metameric relations is presented by the two classes of alcoholic cyanides.

1. *Cyanides.*—By distilling ammonium acetate with phosphoric anhydride (a substance which has an extraordinary affinity for water), the ammonium salt is converted into a volatile body, long known as acetonitril, and boiling at 77°.

$$NH_4C_2H_3O_2 - 2OH_2 = NC_2H_3$$
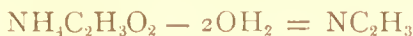
When acted upon by boiling alkali, it yields up its nitrogen in the form of ammonia, and regenerates an acetate.

$$NC_2H_3 + OKH + OH_2 = NH_3 + C_2H_3(OK)O$$
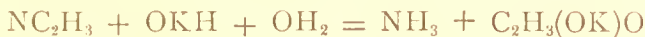
This reaction is explained by supposing that in acetonitril or methyl cyanide the two atoms of carbon are in direct union with each other, as represented by this diagram.

$$N \equiv C - CH_3.$$
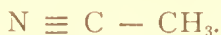
2. *Isocyanides or Carbamines.*—These compounds undergo a different transformation when acted upon by hydrating agents. Notwithstanding that they have the same composition as the cyanides, they are scarcely affected by alkalies, though when boiled with diluted acids they are readily converted into formic acid and bases, in which the nitrogen is associated with part of the carbon. For example, methyl isocyanide treated in this manner yields methylamine and formic acid.

$$NC_2H_3 \quad + \quad 2H_2O = N \left\{ \begin{array}{l} H_2 \\ CH_3 \end{array} \right. + CHO.OH$$
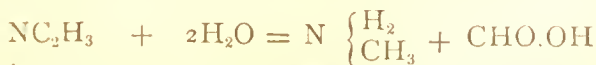
Methyl isocyanide.　　Water.　Methylamine.　Formic acid.

In these compounds, then, the nitrogen probably forms

the link between the two atoms of carbon, in the manner shown by the following graphic formula :—

$$C \equiv N - CH_3$$
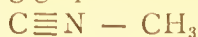
ALLOTROPY.

Many of the elements are known to exist in the form of two or more modifications, which are very different in physical properties and to some extent also in chemical behaviour. One or two examples have been already referred to under the head of physical isomerism and of polymerism. It is probable that a closer examination of the different cases of allotropy known among the elements would enable us to range them all in one or other of these classes. At present, however, our knowledge will not allow us to adopt with any degree of confidence a final decision upon this point.

In the earlier part of this chapter, prismatic sulphur is described as a physical or mechanical modification of the octahedral form of the element, and this is probably correct. But these two are not the only varieties of which this body is susceptible. By heating melted sulphur to a temperature of 240° to 250° it becomes extremely viscid, and if cooled suddenly whilst in this condition the viscid consistency is retained, and the product is a tough elastic solid quite different in aspect from ordinary sulphur. In this state it is insoluble in carbon bisulphide, a liquid which takes up octahedral sulphur very freely.

After keeping a few hours it becomes brittle and crystalline, and recovers its solubility in the usual solvents. The same change may be brought about in a few minutes by plunging it into hot water, and in this way a most interesting phenomenon may be observed. If a considerable quantity be immersed in water a few degrees below the boiling point, the water will be made to boil briskly by reason of the evolution of the heat which is extricated from the plastic sulphur during its conversion into the crystalline.

In these transformations and in the insoluble character of this plastic sulphur, we may trace a close resemblance to the modifications to which certain carbon compounds, such as aldehyd, cyanic acid, and other bodies, are subject, and which are known to be the effect of polymeric changes. It seems not unreasonable to consider that the production of plastic sulphur may be brought about in the same way.

Phosphorus presents us with an example of a somewhat similar kind. This element in its ordinary state is at common temperatures a solid of waxy consistence, which becomes brittle at low temperatures. Its specific gravity is 1·82. It melts easily, dissolves in carbon disulphide, and by sublimation or solution it may be obtained in brilliant crystals in the form of regular octahedrons and dodecahedrons. When this body is heated to a temperature approaching 250° it is slowly transformed into a dull red powder or mass, of specific gravity 2·14, which is no longer soluble in carbon disulphide. It shows itself also in many ways less inclined to enter into chemical combination than common phosphorus, being far less easily inflammable and oxidisable, and unaffected by hot alkaline solutions.

The explanation of this appears, at least very probably, to be that the molecules of the ordinary phosphorus combine together into more complex groupings to form the allotropic molecules, and so expend part of their chemical energy. How to reconcile with this view the fact that heat is absorbed and not evolved in the process is, however, not very clear.

Carbon is another element which assumes several distinct forms, the relations of which are of great interest. We may divide these various modifications into two distinct groups, the crystalline and amorphous.

Crystalline carbon is dimorphous. In one form it constitutes the diamond, which crystallises in octahedral forms of the regular system, and has a specific gravity on the average of 3·3. The other is graphite, or, as it is frequently

called, plumbago or black lead, the crystalline form of which, hexagonal plates, is quite incompatible with the form of the diamond.   The average specific gravity of graphite is 2·2. If now we review the results which have been obtained by burning the different forms of crystalline carbon, we find that, allowing for slight experimental errors, the amount of heat evolved by the combustion of equal weights of diamond and graphite are practically the same.   Twelve grams of each substance burnt in excess of oxygen disengage enough heat to raise the temperature of about 93,300 grams of water one degree, or as it is usually expressed, 93,300 units of heat are evolved.   The exact numbers in each case are as follows :—

Diamond	.	.	.	.	93240
Natural graphite	.	.	.	.	93560 } mean
Graphite from iron		.	.	.	93140 } 93350.

The smallness of the difference observed would lead one to the belief that graphite and diamond possess the same atomic structure, and that they owe their peculiarities to different arrangement of their molecules—that in short they belong to the class of physical isomerides, were it not for some remarkable facts in connection with their behaviour under the influence of chemical reagents.   A mixture of nitric acid and potassium chlorate has no action on the diamond, even in the state of the finest dust, but under the influence of this powerful oxidising mixture, graphite is converted into a yellow crystalline substance, called by Sir B. Brodie, who discovered it, graphic acid.   This compound contains $C_{11}H_4O_5$ (Brodie), and when heated it decomposes violently, leaving a black graphitic residue, which still retains oxygen and hydrogen.

Amorphous carbon may be obtained by a great variety of processes, and in each case the product exhibits more or less distinctly marked peculiarities.

But neither vegetable nor animal charcoal, lamp-black,

coke, nor gas carbon yields by the action of potassic chlorate any substance of the nature of graphic acid, but only black soluble substances of indefinite composition. Twelve grams of wood charcoal give out 96,960 units of heat when burnt so as to form carbonic anhydride, and other kinds of charcoal when deprived as completely as possible of hydrogen and oxygen, give numbers closely agreeing with this. Taking the average heat of combustion of crystalline carbon as 93,300 units, it is obvious that there is too great a difference here to be fairly accounted for by the hypothesis of experimental error, and consequently that there is some essential difference in the constitution of crystalline and amorphous carbon. The question whether this difference is sufficient to indicate a polymeric relation between these bodies remains to be answered. Silicon and boron form allotropes, which are analogous to those of carbon, and concerning which the same questions may be propounded.

The study of a great number of cases has led to the discovery that the formation of any two isomeric bodies always involves the consumption of different amounts of heat. Also, that when these bodies are burnt, or otherwise similarly decomposed, the disruption of their molecules is attended by the evolution of different amounts of heat.

This is nearly equivalent to saying that in order to produce equal weights of two isomerides different amounts of work must be expended in the two processes, and that different amounts of energy are stored up in the products.

How is this energy disposed of? According to one view, and adopting the molecular theory, we may reply that the energy is employed in communicating to some atom or atoms within the molecule a new kind of motion whereby it acquires new chemical functions, and this change we figure to our minds, and render intelligible by the hypothesis that in the transformation of a body into its isomeride, the position of certain atoms contained within the molecule is

M

changed. We endeavour to represent this change of function by altering the arrangement of the symbols which go to make up the formula of the body. Examples of this will be found freely scattered through these pages ; but as an additional illustration, we might refer to an interesting case of isomeric change observed not long ago by Hofmann.

It was found that methyl-aniline,

$$(C_6H_5)' \!\!-\!\! N \!\!<\!\!\begin{array}{l} CH_3 \\ H \end{array}$$
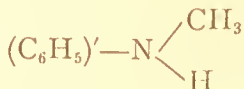
by protracted heating to a high temperature, is converted into toluidine,

$$(CH_3)\!\!-\!\!(C_6H_4)'' \!\!-\!\! N \!\!<\!\!\begin{array}{l} H \\ H \end{array}$$
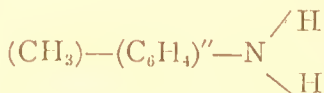
In this metamorphosis an atom of hydrogen and an atom of methyl, CH_3, appear to exchange functions, and in order to record this exchange the formulæ are written in the above or some similar manner, though it by no means follows that we are to infer an exchange of *place*.

But in expending energy upon some part of a molecule, it is not very probable that the energy of the molecule as a whole remains unaltered. Still, it is conceivable that in some cases it may be so, and a careful comparison of the chemical properties of a great many pairs of isomeric bodies would be of the highest interest, as in this way we might arrive at a solution of the question, whether bodies possessing a great store of energy are really more active in their chemical behaviour than others in the production of which a smaller amount of energy has been consumed.

EXERCISES ON SECTION III.

1. One atom of antimony is said to be equivalent to three, and one atom of zinc to two, atoms of sodium. Explain this statement.

2. Distinguish between atomic, equivalent, and molecular weights.

Give the atomic and equivalent weights of mercury, zinc, chlorine, iodine, sulphur, iron, and copper.

Also write down the molecular weights of H_2S, PCl_5, AsH_3, H_2SO_4.

3. What weight of sulphuric acid can be precipitated by one gram of barium chloride ?

4. What is the weight and volume (at normal temperature and pressure) of the hydrogen contained in 10 grams of microcosmic salt, $NaNH_4HPO_4.4H_2O$?

5. Enumerate very briefly the various methods by which atomic weights may be determined ; and indicate in the case of each of the following elements the method or methods which would be applicable— oxygen, chlorine, potassium, mercury, carbon, sulphur, lead, silver, arsenic, silicon, barium, copper, manganese.

6. The specific heat of iron is ·1138. State approximately its atomic weight.

7. The specific heat of cadmium is ·0567, and its equivalent 56. Give its atomic weight.

8. The equivalent of platinum is 49·4, and its perchloride has the formula $PtCl_4$. Find its specific heat.

9. The formula of water was formerly written thus, HO, and subsequently, for some years, H_2O_2 (assuming O=8). Discuss both these formulæ, pointing out any inconsistencies you may detect in them.

10. Complete the equation,

$$Ag_2O \;+\; H_2O_2 =$$
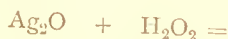
Quote analogous reactions and explain the theoretical significance of these facts.

11. The volume of the molecule of a compound body in the gaseous state is double the volume of the atom of hydrogen. Examine the truth of this statement ; give the experimental facts upon which it is based, and discuss any exceptions to it with which you are acquainted.

12. Acetic acid contains C 40·0, H 6·6, and O 53·4 per cent.; and chloracetic acid contains 37·5 per cent. of chlorine. Calculate the molecular weight of acetic acid.

13. Explain the signification of the several formulæ for potassic sulphate,

$$K_2O.SO_3 \;; \; \left. \begin{array}{l} KO \\ KO \end{array} \right\} SO_2 \;; \; K_2SO_4$$

and

$$\begin{array}{c} O \quad \; O-K \\ \diagdown\!\!\!\backslash \;\; \diagup \\ S \\ \diagup\!\!\!\!/ \;\; \diagdown \\ O \quad \; O-K \end{array}$$
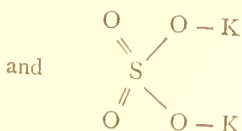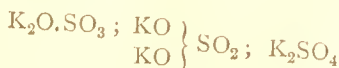
14. What is understood by the terms *valency* and *atomicity* respectively, and how would you ascertain the valency and atomicity of a given element, for example, of carbon or phosphorus ?

15. What is the atomicity of each of the following radicles :—

S, O, Cl, OH, NH_4, NH_3, NH_2, NH, N, N_2, PO, SO_2?

16. With the help of the table on page **152** write down the formulæ of the following salts :—Sodium fluoride, silver sulphate, mercuric cyanide, mercurous phosphate, barium chlorate, bismuth chloride, ferrous orthosilicate, cupric acetate, ferric nitrate, chromic oxalate, stannic phosphate, calcium hypochlorite, etc. etc.

17. The density of the vapour of ammonium chloride is said to be abnormal.   Explain this statement, and give as far as you can experimental evidence in support of this view.

18. Define in a few words the terms *allotropy, metamerism, polymerism*.

19. A current of electricity is passed simultaneously through solutions of cupric and cuprous chloride.   How much copper and how much chlorine are liberated from the cuprous chloride for every molecule of cupric chloride decomposed by the current?   In what relation do these quantities stand to the quantity of zinc consumed in each cell of the battery, secondary actions being neglected ?

20. The atomic weight of silver being **108**, and its specific heat ·057, another metal M, of which **70** parts unite with 35·5 parts of chlorine, is found to have the specific heat ·0306.   What is the atomic weight of this metal and the formula of its chloride ?

21. Give reasons for representing hydrobromic acid by a formula similar to that of hydrochloric acid ; HCl, HBr.

22. Alcohol, ether, and acetic ether have the following rational formulæ,

$$\left. \begin{matrix} C_2H_5 \\ H \end{matrix} \right\} O \ , \qquad \left. \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \right\} O \ , \qquad \left. \begin{matrix} C_2H_5 \\ C_2H_3O \end{matrix} \right\} O$$

What arguments could you draw from the existence of such bodies in favour of the number **16** as the atomic weight of oxygen ?   Why is it probably neither 8 nor 32 ?

23. The formula of the molecule or chemical unit of ammonia is NH_3 What is the meaning of this formula, and what are the reasons for choosing it ?

24. A compound is found by analysis to have the following composition : —

Carbon	.	.	.	.	.	.	. 52·18
Hydrogen	.	.	. .	.	.	.	. 13·04
Oxygen	.	.	.	.	.	.	. 34·78
							100·00

To find its simplest formula.

25. The analysis of a compound leads to these numbers—

Carbon	.	.	.	.	.	.	. 37·20
Hydrogen	.	.	.	.	.	.	. 7·90
Chlorine	.	.	.	.	.	.	. 54·95
							100·05

It is not often that the formula can be calculated so easily as in the example given in the text and in the last exercise. It must be borne in mind that in actual practice a slight loss is incurred in the estimation of many elements. The number for hydrogen, however, generally comes out a trifle too high. Oxygen is always estimated by taking the difference between the total weight of the body analysed, and the sum of the weights of the constituents which have been actually weighed.

In the present example we proceed in the following manner :-

Divide the percentages by the atomic weights in the usual way :

$$\frac{37\cdot2}{12} = 3\cdot1 \text{ atoms of carbon.}$$

$$\frac{7\cdot9}{1} = 7\cdot9 \text{ ,, ,, hydrogen.}$$

$$\frac{54\cdot95}{35\cdot5} = 1\cdot54 \text{ ,, ,, chlorine.}$$

Divide the three quotients by the last, which is the least.

$$\frac{3\cdot1}{1\cdot54} = 2\cdot01 \text{ atoms of carbon.}$$

$$\frac{7\cdot9}{1\cdot54} = 5\cdot12 \text{ ,, ,, hydrogen.}$$

$$\frac{1\cdot54}{1\cdot54} = 1 \text{ atom of chlorine.}$$

Now recollecting that the percentages found by analysis are not exactly true, but only close approximations to the correct numbers, and remembering that the hydrogen is generally in slight excess, we may

safely reject the two small fractions which occur in the above num-
bers and the formula then reads

$$C_2H_5Cl.$$

To prove that this represents correctly the composition of the body,
it is well to recalculate the percentages on the basis of this formula.
This calculation is performed in the following manner :—

$$C_2 = 12 \times 2 = 24$$
$$H_5 = 1 \times 5 = 5$$
$$Cl = 35\cdot5$$
$$\overline{ 64\cdot5}$$

$$\text{Then } \frac{24 \times 100}{64\cdot5} = 37\cdot20$$

$$\frac{5 \times 100}{64\cdot5} = 7\cdot75$$

$$\frac{35\cdot5 \times 100}{64\cdot5} = 55\cdot03$$

And these theoretical numbers are seen to be very close to those
obtained by experiment.

Theory.							Experiment.
C 37·20	.	.	.	.	.	.	. 37·20
H 7·75	.	.	.	.	.	.	. 7·90
Cl 55·05	.	.	.	.	.	.	. 54·95

26. What is the simplest formula you would assign to a substance
containing—

Carbon	.	.	.	.	.	.	. 54·5
Hydrogen	.	.	.	.	.	.	. 9·2
Oxygen	.	.	.	.	.	.	. 36·3

in 100 parts ?

27. Also to the following body :—

Carbon	.	.	.	.	.	.	. 88·20
Hydrogen	.	.	.	.	.	.	. 11·80
							100·00

28. And again to an organic base containing—

Carbon	.	.	.	.	.	.	. 63·78
Hydrogen	.	.	.	.	.	.	. 5·76
Nitrogen	.	.	.	.	.	.	. 3·32
Oxygen	.	.	.	.	.	.	. 27·14
							100·00

29. From the following percentages calculate formulæ for the several
compounds :—

Magnetic Iron Pyrites.

| Iron | . | . | . | . | . | . | . | 59·72 ⎫ |
| Sulphur | . | . | . | . | . | . | . | 40·22 ⎭ |

Iron Peroxide.

| Iron | . | . | . | . | . | . | . | 70 ⎫ |
| Oxygen | . | . | . | . | . | . | . | 30 ⎭ |

Hydrogen Peroxide.

| Hydrogen | . | . | . | . | . | . | 5·88 ⎫ |
| Oxygen | . | . | . | . | . | . | . | 94·12 ⎭ |

Cryolite.

Sodium	.	.	.	.	.	.	32·79 ⎫
Aluminium	.	.	.	.	.	.	13·02 ⎬
Fluorine	.	.	.	.	.	.	54·19 ⎭

Mannite.

Carbon	.	.	.	. .	.	.	39·31 ⎫
Hydrogen	.	.	.	.	.	.	7·71 ⎬
Oxygen	.	.	.	.	.	.	52·98 ⎭

Benzoic Acid.

Carbon	.	.	.	.	.	.	68·67 ⎫
Hydrogen	.	.	.	.	.	.	4·95 ⎬
Oxygen	.	.	.	.	.	.	26·38 ⎭

Caffeine.

Carbon	.	.	.	.	.	.	49·05 ⎫
Hydrogen	.	.	.	.	.	.	5·14 ⎬
Nitrogen	.	.	.	.	.	.	28·61 ⎬
Oxygen	.	.	.	.	.	.	17·20 ⎭

Cane Sugar.

Carbon	.	.	.	.	.	.	42·00 ⎫
Hydrogen	.	.	.	.	.	.	6·46 ⎬
Oxygen	.	.	.	.	.	.	51·54 ⎭

Uric Acid.

Carbon	.	.	.	.	.	.	35·71 ⎫
Hydrogen	.	.	.	.	.	.	2·38 ⎬
Nitrogen	.	.	.	.	.	.	33·33 ⎬
Oxygen	.	.	.	.	.	.	28·58 ⎭

30. Find the formula of nitrosoterpene from these numbers—

Carbon	.	.	.	.	.	$72 \cdot 57$
Hydrogen		.	.	.	.	$8 \cdot 97$
Nitrogen	.	.	.	.	.	$8 \cdot 74$

in 100 parts,

and for nitrosoterpene hydrochloride from the following percentages:

Carbon	.	.	.	.	.	.	$59 \cdot 58$
Hydrogen	.	.	.	.	.	.	$8 \cdot 07$
Nitrogen	.	.	.	.	.	.	$7 \cdot 20$
Chlorine	.	.	.	.	.	.	$17 \cdot 45$

31. The silver salt of an organic acid was found by analysis to yield $47 \cdot 1$ per cent. of metallic silver. Determine its molecular weight. In the formation of the silver salt from the acid, 108 parts of silver take the place of 1 part of hydrogen. Therefore,

Molec. wt. of acid $- 1 =$ molec. wt. of salt $- 108$

or   Molec. wt. of acid $=$ molec. wt. of salt $- 108 + 1$

In the example given $47 \cdot 1$ parts of silver are contained in 100 parts of the salt. So that 108 parts of silver are contained in $\dfrac{108 \times 100}{47 \cdot 1} = 229 \cdot 3$ parts of the salt. This is, therefore, a number identical with, or very near to, its molecular weight. The answer is, therefore,

Molec. wt. required $= 229 \cdot 3 - 108 + 1 = 122 \cdot 3$.

Or, since the atomic weights of carbon, hydrogen, oxygen, and nitrogen are all integers, the fraction must be discarded, and the number becomes 122.

This corresponds with the formula of benzoic acid ; verify it.

32. Aniline contains—

Carbon	.	.	.	.	.	.	$77 \cdot 4$
Hydrogen		.	.	.	.	.	$7 \cdot 5$
Nitrogen	.	.	.	.	.	.	$15 \cdot 0$

per cent.

and its platino-chloride contains $32 \cdot 9$ per cent. of platinum, to find its molecular weight and formula.

As explained in Chapter XVI., p. 127, the platinum salts of nitrogenous bases are constituted on the same type as that of ammonia. Hence we may represent the formula of platino-chloride of aniline thus,

$$2(\text{Aniline} + \text{HCl}) + \text{PtCl}_4$$

or $$\text{Aniline} + \text{HCl} + \frac{\text{PtCl}_4}{2}$$
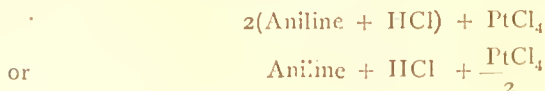
The first question then is, what weight of platinum salt is repre-sented by this formula.   This is answered as follows : —

32·9 parts of platinum make 100 parts of platinum salt,

therefore 197·5 parts or one atom of platinum make $\dfrac{100 \times 197·5}{32·9}$

parts, or 600.

We have now to subtract from this the platinum perchloride and hydrochloric acid ; half the remainder is the molecular weight of the aniline.

$$600 - 339·5 - 73 = 187·$$
and
$$\frac{187·5}{2} = 93·7$$

Now, taking the percentage composition of aniline, we have to calculate the proportions of the three elements contained in 93·7 parts of the base.

$$100 : 93·7 : : 77·4 : x$$
$$x = 72·5 \text{ carbon.}$$
$$100 : 93·7 : : 7·5 : v$$
$$y = 7·0 \text{ hydrogen.}$$
$$100 : 93·7 : : 15·0 : z$$
$$z = 14·0 \text{ nitrogen.}$$

Hence the formula is obtained by dividing these numbers by the respective atomic weights.

$$\frac{72·5}{12} = 6·04 \text{ atoms of carbon.}$$

$$\frac{7·0}{1} = 7 \text{ atoms of hydrogen.}$$

$$\frac{14·0}{14} = 1 \text{ atom of nitrogen.}$$

Hence, allowing for experimental error, which in this case is very small, the molecular formula required is

$$C_6H_7N.$$

33. ·1442 gram of anthraflavic acid gave ·3712 gram of CO_2 and ·0448 gram of water.   Calculate a formula.

34. A sulphide of tellurium and arsenic was analysed.   ·6347 gram of the mineral gave ·2584 gram of tellurium, ·3978 gram of ammonio-magnesium arsenate ($MgNH_4AsO_4.H_2O$), and 1·6453 gram of barium sulphate.   Calculate a formula.

35. The analysis of trichloracetyl urea gave the following results :—

    (a) ·3210 gram gave ·2060 gram of CO_2 and ·0453 gram of H_2O ;
    (b) ·0825 gram gave ·0109 gram of nitrogen ;
    (c) ·1204 gram gave ·2510 gram of AgCl.

Calculate the formula of the compound.

36. Analysis of uranium pentachloride :—

Weight of substance taken	.	.	.	·8955 gram
,, ,, U_3O_8 found	.	.	.	·6038 ,,
,, ,, AgCl ,,	.	.	.	1·4997 ,,

Calculate the formula.

37. ·3807 gram of benzoic acid gave ·9575 gram of CO_2 and ·1698 gram of water. And ·4287 gram of benzoate of silver gave ·2020 of silver. Calculate the rational formula of benzoic acid.

38. ·5828 gram of platino-chloride of caffeine left after ignition ·143 gram of platinum. What are the molecular weight and formula of caffeine, which contains

Carbon	.	.	.	.	.	.	49·05
Hydrogen	.	.	.	.	.	.	5·14
Nitrogen	.	.	.	.	.	.	28·61
Oxygen	.	.	.	.	.	.	17·20

per cent.

39. The platinum salt of a volatile organic base was found by analysis to have the following percentage composition :—Carbon, 9·5 ; hydrogen, 3·2 ; nitrogen, 5·7 ; chlorine, 42·0 ; and platinum, 39·0. The vapour density of the base was found to be 1·59 (air = 1). Calculate from these data its molecular formula.

40. The silver salt of an organic acid contained 62·44 per cent. of metallic silver. It also contains 17·34 per cent. of carbon and 1·73 per cent. of hydrogen. From these data endeavour to find a formula for the acid.

SECTION IV.

———◦◦———

CHAPTER XXI.

CLASSIFICATION OF ELEMENTS.

THE following list includes all but seven rare metallic elements, the consideration of which, obscure as their characters are, is unnecessary in a work like this. The numbers in the table represent the specific gravities of those which are solid, usually in the densest form in which they are known.

     I.—*Non-metallic or Oxygenic* Elements.*

      Gaseous.

        O, N, F (?), Cl (liquid 1·33).

      Liquid.

        Br. 2·96

      Solid.

        S (octahedral) 2·07
        P (red)   . 2·2
        Si (graphitic) 2·49
        B (adamantine) 2·68
        C (adamantine) 3·5
        Se (crystalline) 4·5
        I   .   ·4·95

* Oxygenic = acid-producing.

II.—*Metalloids or Imperfect Metals.*

Gaseous.

H.

Solid.

Zr	.	4·15
V	.	5·5
As	.	5·9
Te	.	6·25
Sb	.	6·8
Sn	.	7·3
Mo	.	8·6
Bi	.	9·8
W	.	17·6
U	.	18·4
Ti , Nb , Ta ?		

III.—*Metals or Basigenic* Elements.*

Li	.	·578
K	.	·865
Na	.	·97
Rb	.	1·52
Cs	.	?
Mg	.	1·7
Ca	.	1·8
Sr	.	2·5
Al	.	2·6
Ba	.	4·0
Cr	.	6·8
Zn	.	7·0
In	.	7·2
Fe	.	7·8
Mn	.	8·0
Ni	.	8·6

* Basigenic = base-producing.

Cd	.	.	8·7
Cu	.	.	8·9
Co	.	.	8·9
Ag	.	.	10·53
Ro	.	.	11·0
Pb	.	.	11·36
Ru	.	.	11·4
Pd	.	.	11·8
Tl	.	.	11·9
Hg	(liquid at 0°)		13·596
Au	.	.	19·34
Os	.	.	21·4
Ir	.	.	21·15
Pt	.	.	21·5

This division into three groups is adopted here for purposes of convenience, but the student must not infer that it is absolutely necessary. Indeed, as he goes on he will find that, as in all attempts to classify the things of nature, it is impossible to define precisely a border-line separating a given class of bodies from all others.

Division I.—Non-metals.

These elements, as a class, are characterised by no generality of physical properties. Three are incondensable gases, fluorine (?), oxygen, nitrogen ; one, chlorine, is gaseous at ordinary temperatures, but liquefiable under pressure ; one, bromine, is a liquid ; the rest are brittle solids. Of these, iodine, sulphur, selenion, and phosphorus are fusible and vaporisable, the remaining three are distinguished by infusibility (?), absolute fixity, even at the highest attainable temperatures, by abnormal specific heats (Chap. XV., p. 114), and by furnishing, in the cases of graphitic carbon and silicon, the only examples among the non-metals of electric conductivity.

In their chemical characteristics, however, there is toler-

able uniformity. They all, except boron*, combine with hydrogen; all, except fluorine, combine with oxygen, often in several proportions, and their oxides are either neutral and indifferent bodies, like carbonic oxide, or, the great majority, anhydrides, which by uniting with water form acids.

NON-METALS.—CLASS I.—THE HALOGENS.

$$
\begin{array}{llll}
\text{Fluorine} & . & . & F = 19 \\
\text{Chlorine} & . & . & Cl = 35\cdot5 \\
\text{Bromine} & . & . & Br = 80 \\
\text{Iodine} . & . & . & I = 127
\end{array}
\left. \vphantom{\begin{array}{l} \\ \\ \end{array}} \right\} \frac{Cl + I}{2} = 81\cdot25
$$

These elements are characterised by a remarkable family resemblance. The three last especially are constantly associated together in nature in the haloid† salts of potassium, sodium, etc., and in the ores of mercury, silver, and other heavy metals. They also agree very closely with one another in their general physical characters and chemical deportment.

At ordinary temperatures chlorine is gaseous, bromine liquid, iodine solid ; but bromine and iodine are volatile and yield heavy, coloured vapours, which, when largely diluted with air, have nearly the same odour as chlorine. Each forms with hydrogen a strongly acid compound, which under ordinary conditions is a colourless, fuming, very soluble gas, consisting of equal volumes of hydrogen and the vapour of the halogen, united without contraction. The chlorides, bromides, and iodides of the alkali metals crystallise in the same form, and the isomorphous replacement of the one halogen by another is observed in a great many other cases.

The following table exhibits the formulæ of all the known oxides and acids of chlorine, bromine, and iodine, from which it will be seen that although there are many gaps to

---

* Hydride of boron is not known, but the organo-boron compounds $B(CH_3)_3$, $B(C_2H_5)_3$ may be considered to represent it.

† ἅλς = sea-salt = common salt.

be filled up perhaps by future research, the correspondence, so far as it goes, is complete :

Halogen Oxides and Corresponding Acids.

$$Cl_2O \quad Cl_2O_3 \quad Cl_2O_4$$

$$HCl \quad HClO \quad HClO_2 \quad \left.\begin{array}{c} HClO_2 \\ HClO_3 \end{array}\right\} \quad HClO_3 \quad HClO_4$$
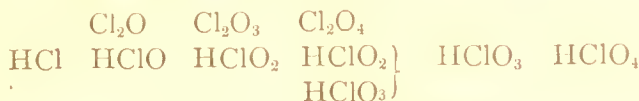
No oxide of bromine known.

$$HBr \quad HBrO \qquad\qquad\qquad HBrO_3 \quad HBrO_4$$
$$\qquad\qquad\qquad\qquad\qquad\qquad I_2O_5 \quad I_2O_7$$
$$HI \quad HIO \,(?) \qquad\qquad\qquad HIO_3 \quad HIO_4$$

The differences exhibited by chlorine, bromine, and iodine are strictly gradational : chlorine, with the smallest atomic weight, being most active, bromine next, and iodine the least energetic of the three. These differences are manifested by their relative affinities for the metals and hydrogen, chlorine displacing bromine, and bromine displacing iodine from such combinations.

Indications of the same differences are afforded by the superior activity of chlorine as a bleaching agent, and by the energy with which it replaces hydrogen in carbon compounds. As in several other cases of nearly allied elements, to be referred to hereafter, the chemical activity diminishes in proportion to the increase of the atomic weight, and rise of boiling-point and specific gravity. (Chap. IV., p. 22.)

The replacement of one or more atoms of hydrogen in a hydrocarbon by an equivalent quantity of one of the halogens, produces a neutral substitution compound ; but if a similar replacement is effected in the molecule of a body which contains oxygen, the product not unfrequently presents well-marked acid properties. This is the case, for example, with some of the derivatives of phenol.

This oxygenic tendency of the halogens is also indicated by the destruction of basic character in the amines or compound ammonias by the substitution of chlorine, bromine,

or iodine for their hydrogen, as is well shown by the chlorinated derivatives of aniline.

Aniline C_6H_7N, a powerful base.

Chloraniline C_6H_6ClN, less basic than aniline.

Dichloraniline $C_6H_5Cl_2N$, feeble base.

Trichloraniline $C_6H_4Cl_3N$, neutral.

Iodine.—Iodine presents one or two peculiarities which deserve special notice, as they serve to remove it to some slight extent from immediate association with the kindred elements, bromine and chlorine. In the first place, its affinity for hydrogen is decidedly less energetic than that of either of the other two elements. This is indicated first by the fact that iodine does not usually bleach vegetable colours; secondly, that, acting alone, it is incapable of producing ubstitution derivatives from carbon compounds.* Whenever substitution of chlorine, bromine, or iodine occurs, the hydrogen which is necessarily eliminated goes to form the corresponding hydracid. Now, in the case of iodo-substitution compounds, it has been shown that they are all decomposed by the action of hydriodic acid, with reproduction of the original body and free iodine. Hence iodosubstitution compounds cannot be formed by the action of iodine, unless precautions are taken to remove or to destroy the hydriodic acid that may be produced. This is effected in various ways, usually by the action of mercuric oxide or iodic acid. The difficulty may also be got over in some instances by substituting iodine monochloride for iodine. Thus orcin acted upon by a solution of iodine chloride gives triiodorcin and hydrochloric acid,

$$C_7H_8O_2 + 3ICl = C_7H_5I_3O_2 + 3HCl.$$
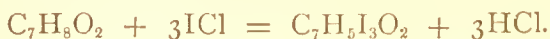
Another distinguishing characteristic of iodine is the intense colour exhibited by the vapour of the element itself, by its solutions in certain liquids, notably in carbon disulphide

* See also Chap. XIII., p. 87. Heat of combination of iodine with hydrogen.

by its compound with starch, and by many iodides, the corresponding chlorides or bromides being either colourless or very pale.

Again, chlorine and bromine are more soluble in water than iodine, and are even capable of forming at low temperatures crystalline hydrates, having the formulæ $Cl_2 10H_2O$, and $Br_2 10H_2O$, no such compound being formed by iodine. On the other hand, the solubility of chlorine and bromine is not appreciably increased by the addition of a chloride or bromide to the water in which they are to be dissolved. Iodine, however, is freely soluble in iodide of potassium, and indeed produces in this way a black liquid which probably contains an unstable triiodide of potassium, KI_3. This compound is not known in the solid state, although analogous periodides are formed by the organic ammonium bases, some of which form crystals of great beauty. The following compounds, for example, containing the alkaloid caffeine, were examined by the author some years ago.

$$(C_3H_{10}N_4O_2H)I_3$$
Caffonium triiodide.

$$(C_3H_{10}N_4O_2CH_3)I_3$$
Methyl-caffonium triiodide.

$$(C_8H_{10}N_4O_2C_2H_5)I_3$$
Ethyl-caffonium triiodide.

The iodates exhibit some anomalies for which there is no parallel among the chlorates. Thus, in addition to the normal potassic iodate, KIO_3, there are two other well crystallised salts, containing an excess of anhydride, for which it is difficult to find analogues, except, perhaps, among the chromates.

Iodates.	Chromates.
KIO_3	
or $K_2I_2O_6$	K_2CrO_4
$K_2I_2O_6.I_2O_5$	$K_2CrO_4.CrO_4$
$K_2I_2O_6.2I_2O_5$	$K_2CrO_4.2CrO_3$

This tendency of iodine to accumulate in its compounds is just one of those characters which belongs especially to polyatomic elements, among which iodine seems, on the whole, entitled to be placed.

Fluorine.—This element has not at present been satisfactorily isolated, but there can be little doubt that it is a gas, probably colourless, having properties similar to those of chlorine or oxygen, but much more strongly marked. Fluorine is connected with the other halogens by the correspondence of hydrofluoric with hydrochloric acid, and by the isomorphism of the fluorides and chlorides. It is, however, widely separated from them, partly in consequence of its very extraordinary attraction for silicon, partly by the non-existence of any oxide or oxyacid of fluorine. In spite also of their general resemblance to the chlorides, bromides and iodides, individual fluorides differ in many cases from the corresponding chlorides. Thus fluoride of calcium is insoluble, chloride of calcium very soluble and deliquescent ; fluoride of silver is soluble in water, chloride of silver totally insoluble ; fluoride of potassium soluble in water, but, unlike the neutral stable chloride, it yields an alkaline solution which probably contains caustic potash and the double hydrogen and potassium fluoride.

$$2KF + OH_2 = KOH + KF.HF.$$
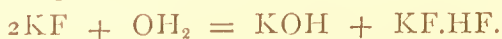
The tendency to produce double salts of this kind has, indeed, led to the idea that fluorine may be really a diatomic element, like oxygen, with the atomic weight 38. The formulæ of the double fluorides would then be comparable with those of oxygen compounds.

Fluorides.			Oxides.
H_2F	analogous to		H_2O
KHF	,,	,,	KHO
KBF_2	,,	,,	KBO_2
K_2SiF_3	,,	,,	K_2SiO_3
K_2SnF_3	,,	,,	K_2SnO_3
etc.			etc.

These double fluorides, however, are not more numerous or prominent than are the double chlorides, bromides, and iodides, and it seems not unreasonable to explain their existence by a similar hypothesis. The atom $F(=19)$ may be occasionally trivalent. If so, the constitution of fluoride of potassium and hydrogen may be represented as

$$KF = FH,$$

and that of the other fluorides, single and double, in a similar manner.

Atomicity of the Halogens.—An atom of a halogen never replaces, in a direct manner, more than one atom of hydrogen. It must also be admitted that, in the haloid salts of these elements, 35·5 parts of chlorine and equivalent quantities of bromine, iodine, and fluorine, are almost always combined with the metallic representative of one part by weight of hydrogen. The halogens are therefore generally univalent. Nevertheless, many compounds are known, the existence of which can scarcely be accounted for, except upon the hypothesis of their occasional trivalent function.

Thus, in addition to the normal iodides and iodo-substitution compounds,

$$H'I, \quad K'I, \quad Hg''I_2, \quad C_2H_3I'O_2,$$
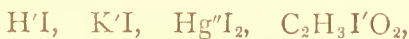
iodine forms the following compounds,

$$I'''Cl_3, \quad I''' (C_2H_3O_2)_3, \quad KAgI'''_2,$$
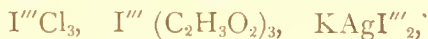
which may be written as follows,
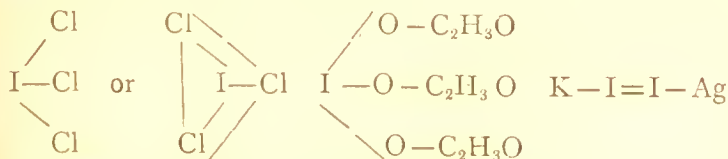
In their oxygenated compounds, chlorine, bromine, and iodine present also a very marked resemblance to nitrogen, which is most generally (perhaps always) a triad. Thus we have hypochlorous and hyponitrous acids, both extremely unstable bodies, known chiefly in the form of their

salts; chlorous and nitrous acids, also very unstable;
chloric and nitric acids, both liquid, easily decomposable,
highly corrosive bodies, the salts of which are all soluble
in water. The nitrogen analogue of perchloric acid is at
present unknown. The formulæ of these corresponding
pairs of compounds are as follows :

$$HClO \qquad HClO_2 \qquad HClO_3 \qquad HClO_4$$
$$HNO \qquad HNO_2 \qquad HNO_3$$

A further correspondence is observable in their oxides,

$$Cl_2O \qquad Cl_2O_3 \qquad Cl_2O_4 \qquad I_2O_5$$
$$N_2O \qquad N_2O_3 \qquad N_2O_4 \qquad N_2O_5$$

Now, if we admit that nitrogen is trivalent in these com-
pounds, the presumption that chlorine and its congeners
are also trivalent is, at least, worthy of discussion. The
following graphic formulæ express the constitution of
chloric and nitric acids upon this hypothesis :—

$$H-O-Cl\diagdown\!\!\!\diagup\genfrac{}{}{0pt}{}{O}{|}{O} \qquad\qquad H-O-N\diagup\!\!\!\diagdown\genfrac{}{}{0pt}{}{O}{|}{O}$$
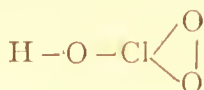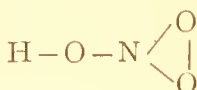
Chloric acid.   Nitric acid.

As contributing evidence in support of the same view,
we might also point to the large number of permanent
and definite double compounds which the chlorides,
bromides, and iodides are capable of forming. We have,
for example, the well-known chloro-platinates of the alkali
metals,

$$2NaCl \cdot PtCl_4$$
$$2KCl \quad \cdot \ PtCl_4, \ etc.$$
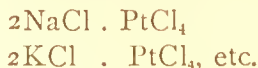
besides the innumerable compounds of the alkali-metal
chlorides with the chlorides of magnesium, iron, aluminium,
mercury, copper, and other metals. Although a few of
these compounds are decomposed by water, the majority of
them are stable enough, and give no signs of alteration by
such treatment. Their constitution is most reasonably

represented upon the assumption of the trivalence of the halogen. The compound $KI.HgI_2$, for example, may be written in this manner.
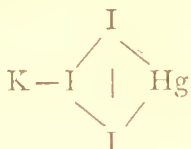
Many chemists regard these compounds as formed by the union of entire molecules of the constituent salts, combined together by some kind of adhesion differing from ordinary chemical affinity. Thus the potassio-mercuric iodide represented above is considered to contain both iodide of potassium and iodide of mercury, $HgI_2 + KI$. It is quite probable that such molecular compounds may exist, but if they do, they might naturally be expected to exhibit something of the appearance and external characters of their proximate constituents. In the case referred to nothing of this kind is observed, the double iodide $KHgI_3$ being a colourless salt, soluble in water, and totally unlike the scarlet, insoluble, mercuric iodide, the elements of which it contains.

<div align="center">NON-METALS.—CLASS 2.</div>

$$
\left.
\begin{array}{lclcl}
\text{Oxygen} & - & O & = & 16 \\
\text{Sulphur} & - & S & = & 32 \\
\text{Selenion} & - & Se & = & 79\cdot5 \\
\text{Tellurium} & - & Te & = & 128
\end{array}
\right\} \frac{S + Te}{2} = 80
$$

These elements are associated together principally by reason of the correspondence in composition and general properties among their compounds with hydrogen,

$$OH_2 \quad SH_2 \quad SeH_2 \quad TeH_2.$$

For although, taking any two adjacent terms of the series, many points of resemblance may be traced out, yet there is a very wide interval between the colourless incondensable

gas oxygen and the silvery, metallic, crystalline, solid tellurium.

Oxygen, standing apart from the rest in virtue of many extraordinary qualities, deserves to be noticed first. This element constitutes nearly one-half the total weight of the earth's crust. Indeed, it seems to be the preponderating element of the globe.

Leaving out of account the insignificant quantities of metals and metallic sulphides embedded in the earth, it may be said that the entire constituents of the earth's crust, including the water of the ocean, consist of compounds . saturated with oxygen, and even supposing all organic bodies to be completely burnt up, the atmosphere would still contain a considerable quantity of unemployed oxygen.

Oxygen is entirely unmatched among the rest of the elements, both as regards the number and varied character of its compounds, and the important part which it plays in relation to combustion and life.

Water, hydrogen protoxide, also exhibits properties which are in every way remarkable as specially fitting it for the part it has to play in the economy of nature. The very type of a neutral body, yet capable, under special circumstances, of acting either as a feeble base or a feeble acid ; an almost universal solvent of saline bodies ; exhibiting the anomaly of attaining maximum density at a temperature $(4°)$ above its solidifying point ; standing alone amongst liquids by reason of its great capacity for heat ; having a vapour-density little more than half that of its gaseous sulphur analogue (SH_2), and yet liquefying and solidifying readily.

The higher oxide of hydrogen, O_2H_2, with its bleaching and oxidising powers, resembles in no slight measure the element chlorine.

The name *oxygen*, " acid producer," from ὀξύς and γεννάω, was given by Lavoisier under the mistaken impression that this element contained a principle common to all acids. This we know was an error. Nevertheless

the name was not ill-chosen, and for the following reasons :—

1. There are many hundreds of acids known, and yet, with about six exceptions, HF, HCl, HBr, HI, HCN, H_2S, all contain oxygen.

2. In proportion as the quantity of oxygen increases in a series of acids containing the same elements, so the acidity as well as the stability of the compound is almost always increased. A detailed examination of such examples as the following would, if space permitted, confirm this statement.

$HClO$	HNO_2	H_2SO_3	H_3PO_2
$HClO_2$	HNO_3	H_2SO_4	H_3PO_3
$HClO_3$			H_3PO_4
$HClO_4$			

Glycollic acid $C_2H_4O_3$
Oxalic acid $C_2H_2O_4$

3. The addition of oxygen to (neutral) aldehyds converts them into acids. Ex. gr.

	Acetic.		
Aldehyd	-	-	C_2H_4O
Acid -	-	-	$C_2H_4O_2$
	Benzoic.		
Aldehyd	-	-	C_7H_6O
Acid -	-	-	$C_7H_6O_2$

4. In homologous series of acids, the lowest terms which are richest in oxygen show a far stronger development of the acid character than the higher terms of the same series, which are comparatively poor in oxygen. Compare for example—

Formic acid, CH_2O_2 containing 69·5 per cent. of oxygen.
Acetic acid, $C_2H_4O_2$,, 53·3 ,, ,,
  with
Valeric acid, $C_5H_{10}O_2$,, 31·3 ,, ,,
  and
Palmitic acid, $C_{16}H_{32}O_2$,, 12·4 ,, ,,

5. Many oxides of metals are basic, that is, saturate acids with production of water and salt, but a few examples will be sufficient to show that it is only those which contain a comparatively small quantity of oxygen that possess this power. As the quantity of oxygen increases in a given series, the basic character gradually disappears, and gives place to a more or less decided acid-forming tendency.

EXAMPLES OF METALLIC OXIDES.

Basic	Hg_2O HgO	K_2O	BaO	PbO	MnO Mn_2O_3 (feebly)	CrO Cr_2O_3(feebly)
Indifferent		K_2O_2 K_2O_4	BaO_2	PbO_2	MnO_2	
Anhydric) Acids)					MnO_3 Mn_2O_7	CrO_3

Allotropic oxygen or ozone is a body which has for some years attracted considerable attention. The experiments of Brodie have finally decided the question of its constitution in favour of the hypothesis long ago put forward by Odling. Ozone is now proved to be allotropic oxygen, free from hydrogen, and to have the formula O_3. It may thus be regarded as formed on the type of hydric peroxide, with which body it agrees in many of its reactions.

Hydric peroxide.   Ozone.

$$H - O$$
$$|$$
$$H - O$$

$$O \diagup O$$
$$| $$
$$\diagdown O$$

Sulphur, Selenion.—These two elements resemble each other closely. Sulphur is a yellow, selenion a red solid, exhibiting several modifications, some of which are crystalline and soluble in carbon disulphide, others amorphous and insoluble.

Principal Allotropes of Sulphur.

		Spec. Grav.	In carbon disulphide.
1.	Octahedral (native)	2·07	soluble.
2.	Prismatic (monoclinic)	1·98	transformed into 1.
3.	Plastic	1·95	insoluble.
4.	Amorphous	1·95	insoluble.

(Precipitated from chloride or theiosulphates.

Principal Allotropes of Selenion.

		Spec. Grav.	In carbon disulphide.
1.	Monoclinic (native)	4·4	soluble.
2.	Crystalline (form?)	4·8	insoluble.
3.	Vitreous	4·3	insoluble.
4.	Amorphous		insoluble.

(Precipitated from selenious acid.)

The following is a comparison of the most important compounds of sulphur and selenion :—

H_2S	SO_2	SO_3	H_2SO_3	H_2SO_4
Gas.	Gas.	Solid.	Crystallisable at low temperatures.	Oily liquid.
H_2Se	SeO_2	SeO_3	H_2SeO_3	H_2SeO_4
Gas.	Solid.	Unknown.	Crystalline solid.	Oily liquid.

The selenates are isomorphous with the sulphates.

The relations of sulphur to oxygen are shown in the following synopsis of some of their compounds :—

SULPHUR.	OXYGEN.
SH_2 gas, feebly acid S_2H_2 oily liquid CS red solid ? CS_2 volatile liquid ⎫ COS gas ⎬	OH_2 O_2H_2 oily liquid CO colourless gas CO_2 gas

ACIDS.	
$C_2H_3O.SH$ theiacetic. B.P. 93° $SO_2.OH.SH$ theiosulphuric	$C_2H_3O.OH$ acetic. B.P. 120° $SO_2.OH.OH$ sulphuric

SULPHUR.	OXYGEN.
BASES.	
SKH	OKH
SK_2	OK_2
SCa	OCa
$CS(NH_2)_2$ sulphurea	$CO (NH_2)_2$ urea
SALTS.	
M'_2CS_3 sulphocarbonate	M'_2CO_3 carbonate
M'_3AsS_4 sulpharsenate	M'_3AsO_4 arsenate
$M'CNS$ sulphocyanate	$M'CNO$ cyanate
ALCOHOLS.	
$S \begin{cases} C_2H_5 \\ H \end{cases}$ mercaptan. B.P. $36°$.	$O \begin{cases} C_2H_5 \\ H \end{cases}$ B.P. $78°·4$
ETHERS.	
$S(C_2H_5)_2$. B.P. $72°$	$O(C_2H_5)_2$ B.P. $35°·6$

It is necessary, however, to add that many oxygen compounds are known for which at present there are no corresponding terms in the sulphur series, the oxides of nitrogen, for example. On the other hand, sulphur has a power of accumulating in a manner which is not exhibited, at least to the same extent, by oxygen. Consequently, many polysulphides exist for which there are no corresponding oxides. Thus we have K_2S_5, CaS_5, FeS_2, $(C_2H_5)_2S_2$ and $(C_2H_5)_2S_3$

Atomicity of Oxygen and Sulphur.

We know of no instance in which oxygen is other than diad, if we except the very curious but imperfectly studied sub-oxide of silver, which is said to have the formula Ag_4O. There are, indeed, two other examples which may be brought forward if we choose to do a little violence to commonly received theories. Carbonic oxide is generally represented as containing unsaturated carbon, $C = O$, but

admitting the essentially tetrad character of the oxygen, we should represent it as constituted thus, $C \equiv O$. Again, water of crystallisation is almost universally considered by chemists to exist as water in the salts in which it occurs, the molecules of the salt and the molecules of the water retaining their individuality, being united only by some kind of adhesion. This is, perhaps, the most rational view, considering the facility with which such water is detached, and the fact that it constitutes no essential part of the chemically reacting unit of the compound in all the most characteristic of its transformations. Nevertheless, the idea that this water is held to the salt by the two extra units of combining power of the oxygen is not wholly preposterous. At any rate, it does away with the difficulty of supposing that in the constitution of a given chemical compound, two different kinds of chemical attraction come into operation, and with the frequent impossibility of referring with any degree of confidence particular cases to the category of atomic or molecular combinations. One example of the application of this hypothesis will suffice. Zinc sulphate contains $ZnSO_4.7OH_2$, or $ZnSO_4OH_2.6OH_2$. This may be expressed in the following manner :—

$$
\begin{array}{c}
\qquad O \qquad\quad O - H \\
\quad \diagup \;\; \diagdown \;\; \diagup \\
Zn \quad \| \quad S \quad \| \\
\quad \diagdown \;\; \diagup \;\; \diagdown \\
\qquad O \quad \| \quad O - H \\
\qquad O \\
\quad \diagup \;\;\; \diagdown \\
H_2 = O \qquad O = H_2 \\
\quad \mid \qquad\quad \mid \\
H_2 = O \qquad O = H_2 \\
\quad \mid \qquad\quad \mid \\
H_2 = O \text{——} O = H_2
\end{array}
$$
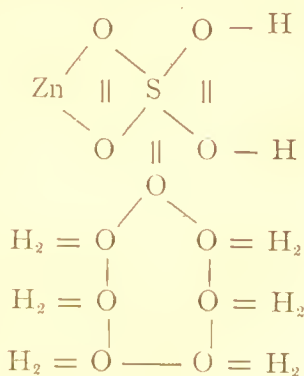
At present, however, and for all practical purposes, it is safest to consider oxygen as invariably diad.

With regard to sulphur, the question is somewhat different. This element forms three well-marked classes of compounds. In the first of these it is bivalent, and may be regarded as the strict representative of oxygen. Examples of this type of compound have been already given, SH_2, S_2H_2, CS_2, COS.

In the second class the sulphur alone is quadrivalent : ex. gr. in*

$$\overset{iv}{S} \begin{cases} Cl \\ Cl \\ Cl \\ Cl \end{cases} \qquad\qquad S \begin{cases} Cl \\ Cl \\ O'' \end{cases} \quad \text{and} \quad S \begin{cases} O'' \\ O'' \end{cases}$$
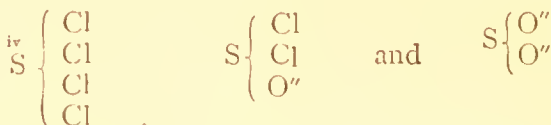
Sulphur tetrachloride.   Theionyl chloride.   Sulphur dioxide.

In the third class of sulphur compounds represented by sulphuric anhydride, SO_3, the central atom seems to be sexi-

valent sulphur ; $\begin{array}{c} O \\ \| \\ O=S=O \end{array}$. It is true that the constitution

of this and all the rest of the sulphur compounds might be represented on the hypothesis that sulphur is diad, $\begin{array}{c} O-S-O \\ \diagdown O \diagup \end{array}$ but the analogy of sulphur with chromium, and especially the isomorphism of the sulphates and chromates, seem to establish the title of sulphur to be regarded as a hexad. The several oxides, hydrates, and oxychlorides are therefore represented in the following manner :—

$$\overset{vi}{S} \begin{cases} O'' \\ O'' \\ O'' \end{cases} \qquad \overset{vi}{S} \begin{cases} O'' \\ O'' \\ Cl \\ Cl \end{cases} \qquad \overset{vi}{S} \begin{cases} O'' \\ O'' \\ (OH)' \\ Cl \end{cases} \qquad \overset{vi}{S} \begin{cases} O'' \\ O'' \\ (OH)' \\ (OH)' \end{cases}$$
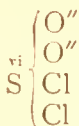
Sulphur trioxide.   Sulphuryl chloride.   Sulphuryl chlorhydrate.   Sulphuryl hydrate, or common sulphuric acid.
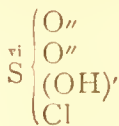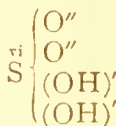
* Sulphur terrachloride is not well known except in combination with metallic chlorides, but the corresponding compounds of selenion and tellurium have been prepared.

$$\overset{vi}{S} \begin{cases} O'' \\ (OH)' \\ (OH) \\ (OH)' \\ (OH)' \end{cases}$$
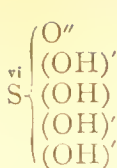
Glacial or tetrahydric sulphuric
acid.

$$\overset{vi}{S} \begin{cases} O \\ O \\ O \\ (OH)' \\ (OH)' \end{cases} \hspace{-1em}\begin{matrix} \\ \rangle Fe \\ \\ \\ \end{matrix}$$

Ferrous sulphate
(dried at 100°).

$$S\,(OH)_6$$

$$S \begin{cases} O \\ O \\ O \\ O \\ O \\ O \end{cases} \begin{matrix} \rangle Hg \\ \\ \rangle Hg \\ \\ \rangle Hg \\ \end{matrix}$$

Orthosulphuric acid
(unknown).
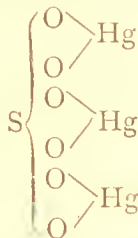
Trimercuric orthosulphate
Turpeth mineral.

$$\begin{cases} SO_2.OH \\ O \\ SO_2.OH \end{cases}$$

Pyrosulphuric, or Nordhausen
sulphuric acid.

$$\begin{cases} SO_2.Cl \\ O \\ SO_2.Cl \end{cases}$$
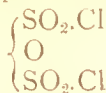
Pyrosulphuryl
chloride.

NON-METALS.—CLASS 3.—BORON.

A triad element, but exhibiting marked analogies with tetrad silicon. The following are their chief points of agreement :—

BORON.	SILICON.
Element, (*a*) amorphous brown powder or (*b*) quadratic octahedrons	Element, (*a*) amorphous brown powder, or (*b*) hexagonal plates
S.G. 2·68	S.G. about 2·5.
BH_3 wanting	SiH_4 spontaneously inflammable gas.
$B(CH_3)_3$, $B(C_2H_5)_3$ etc.	$Si(CH_3)_4$, $Si(C_2H_5)_4$, etc.
$BiCl_3$ B.P. 17°	$SiCl_4$ B.P. 59°
BF_3 gas	SiF_4 gas
$BF_3.HF$ or BHF_4 known only in solution : salts crystallisable.	$SiF_4.2HF$ or SiH_2F_6 scarcely known except in solution : salts tolerably stable.
H_3BO_3 crystallisable.	H_4SiO_4 exists only in solution.

BORON.	SILICON.
HBO_2	H_2SiO_3
B_2O_3 (fused, S.G. 1·83)	SiO_2 (fused S.G. 2·2)
M'_3BO_3 orthoborates	M'_4SiO_4 orthosilicates
$M'BO_2$ metaborates	M'_2SiO_3. metasilicates
Many anhydroborates	Many anhydrosilicates
$M'BO_2 + x\ B_2O_3$	$M'_2SiO_3 + x\ SiO_2$
Ex. fused borax $2NaBO_2 + B_2O_3$	Ex. orthoclase felspar
	$\begin{array}{l} K_2SiO_3 \\ Al_2(SiO_3)_3 \end{array} \Big\} + 2SiO_2$

Boron is one of the few elements which combine in a direct manner with nitrogen. Boron nitride has the formula BN or perhaps B_3N_3.

NON-METALS.—CLASS 4.

Carbon, C = 12.
Silicon, Si = 28.

Allotropes of Carbon.

a. Diamond, octahedral, S.G. 3·3 to 3·5.
b. Graphite, hexagonal, S.G. about 2·2.
c. Charcoal, amorphous.

Allotropes of Silicon.

a. Adamantine (?)
b. Graphitic, hexagonal, S.G. about 2·5.
c. Amorphous.

Carbon is remarkable as being the essential element of organic nature, and silicon as being one of the most abundant constituents of the earth's solid crust. Regarded as chemical elements, they present problems of special interest in their nonconformity to the law of Dulong and Petit (p. 114), and in the multitudinous array of compounds which they have furnished to the chemist. The carbon compounds will be specially considered hereafter ; it therefore only remains to point out in this place a few of the remarkable coincidences of composition so frequently observed

between the compounds of these two elements. The number of bodies in which silicon replaces one or more atoms of the carbon in some already familiar compound is rapidly increasing, and still further developments in this direction may be looked for.

In comparing carbon and silicon compounds together, it cannot be said that the similarity so often noticed in their constitution extends to their properties. In most cases corresponding carbon and silicon compounds are very different bodies. A few examples only can be referred to :—

Carbon Compounds.	Silicon Compounds.
CO	SiO unknown.
CO_2, colourless gas, soluble to some extent in water.	SiO_2, crystalline solid, fusible only at a very high temperature, totally insoluble in water. Hydrates slightly soluble.
CH_4, permanent gas.	SiH_4, spontaneously inflammable gas.
$CHCl_3$, heavy liquid, unacted upon by water.	$SiHCl_3$, liquid, decomposed by water.

Orthosilicic and orthocarbonic acids, H_4SiO_4 and H_4CO_4, are unknown, and but very few of their compounds have been studied. Of orthosilicates we have olivine, Mg''_2SiO_4, ferrous orthosilicate, Fe''_2SiO_4, the ethyl salt $(C_2H_5)_4SiO_4$, and a few others. Orthocarbonates are represented by such compounds as the ammonium-hydrogen orthocarbonate $(NH_4)_2H_2CO_4$ and the ether $(C_2H_5)_4CO_4$. Ordinary carbonates are derived from metacarbonic acid H_2CO_3, a body which has not been isolated, though the corresponding silicic acid has been obtained as a solid glassy mass. All carbonates are decomposed on the addition of even the weakest acids, whereas the majority of the silicates resist the attacks of any but hydrofluoric acid.

Atomicity of Carbon and Silicon.

Silicon is always tetrad. Carbon is tetrad in all its known compounds, except carbonic oxide, CO, and possibly the isocyanides. The unsaturated character of carbonic oxide

is shown by the readiness with which it enters into combi-
nation with chlorine, with oxygen, with potassium, with
caustic potash, and with cuprous or platinous chloride.

$$CO + Cl_2 = COCl_2 \text{ carbonyl chloride}$$
$$CO + O = CO_2 \quad \text{carbon dioxide}$$
$$_nCO + K_n = K_nC_nO_n$$
$$CO + KHO = KCHO_2 \text{ formate, \&c.}$$
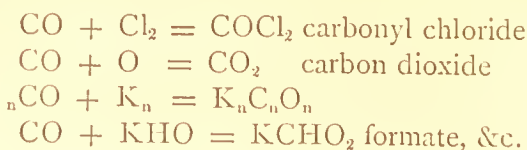
From the characteristic reactions of the isocyanides (see
Isomerism, Chap. XX., p. 157) it appears that in these
bodies an atom of carbon is linked to the hydrogen, or other
positive radicle present, by the atom of nitrogen. Now, ac-
cording as we regard the nitrogen in these compounds as
discharging a triad or pentad function, we must attribute
to the carbon a replacing value equal to two or four atoms
of hydrogen. Either of these two formulæ, then, may be
adopted :—

$$\overset{''}{C} = \overset{'''}{N} - \overset{'}{R} \quad \text{or} \quad \overset{iv}{C} \equiv \overset{v}{N} - \overset{'}{R}.$$
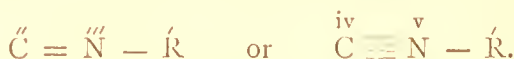
The one may be regarded as a derivative of ammonia,
the other of marsh-gas.

In favour of the former view, we may adduce the combi-
nation of such a cyanide as prussic acid with hydrochloric,
hydrobromic and hydriodic acids, forming crystalline com-
pounds analogous to sal-ammoniac, and with hydrogen form-
ing methylamine ; also the combination of the isocyanides
generally with oxygen to form isocyanates, and with sulphur
to form isosulphocyanates. These combinations may be re-
presented thus—

$$N\begin{cases} H \\ C'' \end{cases} \quad N\begin{cases} H \\ C'' \end{cases} \quad N\begin{cases} H \\ C = O \end{cases} \quad N\begin{cases} H \\ C = S \end{cases} \quad N\begin{cases} H_2 \\ CH_3 \end{cases}$$
$$HCl$$

Hydrocyanic   Carbylamine   Cyanic Acid.   Sulphocyanic   Methylamine
  Acid or   Hydrochloride.   Acid.
Carbylamine.
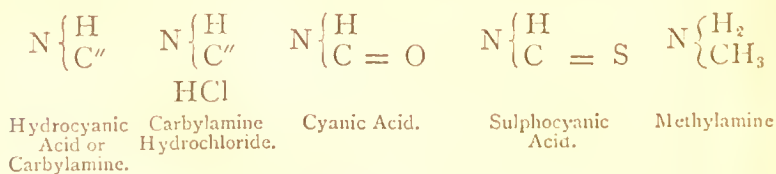
If the second hypothesis is adopted, we must imagine

that the union of the carbon to the nitrogen is partly unlocked before these compounds can be found. Written on the marsh-gas type the formulæ then become—

$$C^{iv}(NH)^{iv} \quad C\begin{Bmatrix} HCl \\ (NH)'' \end{Bmatrix} \quad C\begin{Bmatrix} O'' \\ (NH)'' \end{Bmatrix} \quad C\begin{Bmatrix} S'' \\ (NH)'' \end{Bmatrix} \quad C\begin{Bmatrix} H_3 \\ (NH_2)' \end{Bmatrix}$$
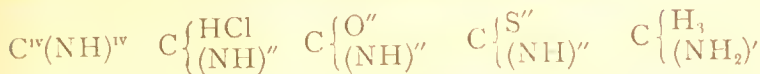
On the whole, the former mode of representation seems the more natural.

NON-METALS.—CLASS 5.—NITROGEN AND PHOSPHORUS.

Nitrogen $N = 14$
Phosphorus $P = 31$ $\dfrac{N + V}{2} = 32 \cdot 5$
Vanadium $V = 51$

Phosphorus $P = 31$
Arsenic $As = 75$ $\dfrac{P + Sb}{2} = 76 \cdot 5$
Antimony $Sb = 122$

Phosphorus $P = 31$
Vanadium $V = 51$ $\dfrac{P + As}{2} = 53$
Arsenic $As = 75$

Phosphorus $P = 31$
Antimony $Sb = 122$ $\dfrac{P + Bi}{2} = 120 \cdot 5$
Bismuth $Bi = 210$

Diagram of numerical relations typical of chemical relations :—

$$\begin{array}{l} N14 \\ | \\ P31 \\ | \\ V51 \end{array} \qquad \left\{ \begin{array}{l} V51 - As75 \\ As75 - Sb122 \\ Sb122 - Bi210 \end{array} \right.$$

Nitrogen is a permanent incondensable gas, which has never been obtained in any other form.

Phosphorus, on the contrary, is, in its ordinary condition, a crystalline solid, though capable of passing into several allotropic modifications. These have already been referred to (Chap. XX.)

The specific gravity of nitrogen agrees with the molecular formula N_2, whilst the vapour density of phosphorus corresponds with P_4. This peculiarity of phosphorus is shared by the semi-metal arsenic.

Both nitrogen and phosphorus are intimately concerned in the processes of animal life, phosphorus being especially abundant in the form of phosphates in bone, and in nervous tissue.

Nitrogen is connected with phosphorus mainly by reason of the resemblance between ammonia NH_3, and phosphine PH_3, and the bases formed from them by substitution of hydrocarbon radicles for the hydrogen. The element itself, as a permanent incombustible gas, is wholly unlike the solid inflammable phosphorus, whilst its oxides and acids, in their volatility and easy decomposability, form a strong contrast to the corresponding compounds of phosphorus. The accident of agreement in their crude or synoptic formulæ by no means implies identity of constitution, and, for the reasons just alluded to, it seems not improbable that the atomic structure of the nitrogen oxides and acids is, at least in many cases, different from that of the phosphorus compounds.

The following are almost the only known examples of concordance in the crude formulæ of the oxygen compounds :—

Nitrogen Trioxide.	Phosphorus Trioxide.
N_2O_3	P_2O_3
Pentoxide	Pentoxide.
N_2O_5	P_2O_5
Nitric Acid.	Metaphosphoric Acid.
HNO_3	HPO_3

The compounds N_2O, NO, N_2O_4, HNO_2 find no parallels in the phosphorus series, whilst H_3PO_4, H_3PO_3, H_3PO_2, $H_4P_2O_7$, the salts of which, at least, are highly stable and definite, are altogether unrepresented among the nitrogen compounds. Again, whilst phosphorus yields two chlorides, PCl_3 and PCl_5, and an oxychloride, $POCl_3$, nitrogen forms no chloride,* but two oxychlorides, $NOCl$, a yellow gas, and NO_2Cl, a volatile liquid. It has been the very general custom to represent all the

* The so-called chloride of nitrogen, obtained by the action of chlorine upon sal-ammoniac, probably contains hydrogen. Its formula is supposed to be $NHCl_2$, but in consequence of its dangerously explosive properties, it has been only imperfectly examined.

compounds of nitrogen by formulæ framed in the same manner as those of the phosphoric compounds, without regard to their dissimilar properties. But by assuming that nitrogen is trivalent in these bodies, we render some account of these discrepancies. On this view the formulæ given above for nitric acid and anhydride may be expanded in the following manner :—

Nitric Pentoxide

$$\begin{matrix} O \\ | \\ O \end{matrix} \Big\rangle N - O - N \Big\langle \begin{matrix} O \\ | \\ O \end{matrix}$$

Phosphoric Pentoxide.

$$O = P - O - P = O$$
$$\quad \| \qquad \quad \|$$
$$\quad O \qquad \quad O$$

Nitric Acid.

$$\begin{matrix} O \\ | \\ O \end{matrix} \Big\rangle N - O - H$$

Metaphosphoric Acid.

$$O = P - O - H$$
$$\quad \|$$
$$\quad O$$
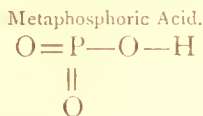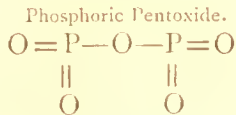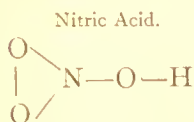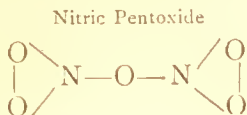
The general fact that bodies in which oxygen is more or less united with oxygen are rather unstable lends some further countenance to this view.*

In the ammonium compounds on the other hand (p. 251), there can be little doubt that nitrogen is pentad, chloride of ammonium, for instance, being $N^V H_4 Cl$.

Phosphorus.—The two chlorides PCl_3 and PCl_5 may be taken as the types of the two chief classes of compounds which phosphorus is capable of forming.

The trichloride PCl_3 is a colourless volatile liquid, which combines in a direct manner with chlorine, with oxygen, or with sulphur, yielding the pentachloride, PCl_5, the oxy-chloride, PCl_3O, and the sulphochloride, PCl_3S, in which compounds the phosphorus appears to be saturated.

The best known iodide is anomalous. It has the formula P_2I_4, and corresponds with a liquid hydrogen compound P_2H_4, to which the spontaneous inflammability of phosphoretted hydrogen is stated to be due.

* The formulæ might also be written $O = N - O - O - O - N = O$ and $O = N - O - O - H$, though for several reasons the form given in the text is preferable.

Phosphine, or phosphoretted hydrogen, PH_3, is a highly inflammable gas, which so far imitates ammonia,* that it combines with hydriodic acid to form a salt, phosphonium iodide PH_4I, crystallisable in cubes.

The compounds in which phosphorus plays the part of a pentad are more numerous. Beside the pentachloride PCl_5, and pentoxide P_2O_5, and intermediate PCl_3O, we have the following series of oxidised bodies which may be considered as derived from phosphine, either by addition of oxygen or by substitution of oxygen for its hydrogen.

Phosphine
H_3P or

$$P\overset{\displaystyle H}{\underset{\displaystyle H}{{-}H}}$$
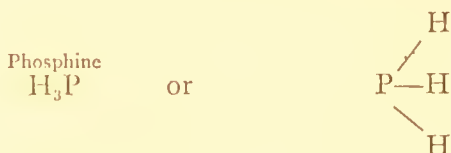
Phosphine Oxide.
H_3PO, unknown, but represented by

Triethyl-phosphine Oxide.
$(C_2H_5)_3PO$ or

$$O{=}P\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_2H_5}{{-}C_2H_5}}$$

Hypophosphorous Acid (monobasic)
H_3PO_2 or

$$O{=}P\overset{\displaystyle OH}{\underset{\displaystyle H}{{-}H}}$$

Phosphorous Acid (dibasic).
H_3PO_3 or

$$O{=}P\overset{\displaystyle OH}{\underset{\displaystyle H}{{-}OH}}$$
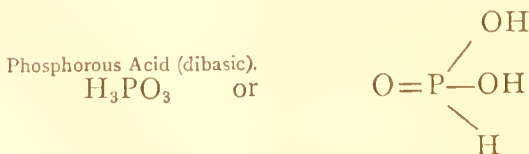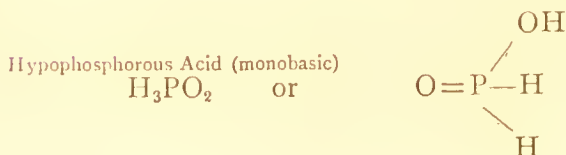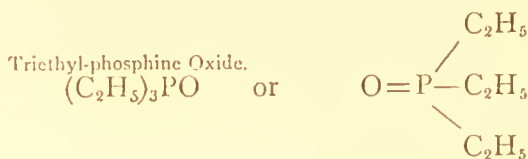
* See also Amines, p. 252.

Orthophosphoric Acid (tribasic)
H_3PO_4 or

$$O=P\begin{matrix} OH \\ -OH \\ OH \end{matrix}$$
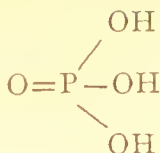
Pyrophosphoric Acid (tetrabasic).
$H_4P_2O_7$ or

$$O=P\begin{matrix} OH \\ OH \end{matrix}$$
$$|$$
$$O$$
$$|$$
$$O=P\begin{matrix} OH \\ OH \end{matrix}$$
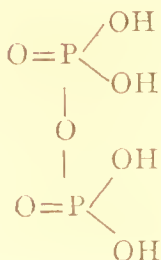
Metaphosphoric Acid (monobasic).
HPO_3

$$O=P\begin{matrix} O \\ OH \end{matrix}$$
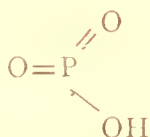
With the exception of the first two compounds in the list, phosphine and its oxide, these bodies are all powerful acids, syrupy, glassy, or crystalline, according to circumstances. They cannot be made to evolve oxygen at any temperature as nitrous and nitric acids do. Under the influence of heat, hypophosphorous and phosphorous acids emit phosphine, leaving a residue of phosphoric acid ;

$$2H_3PO_2 = H_3PO_4 + H_3P$$
$$\text{and } 4H_3PO_3 = 3H_3PO_4 + H_3P,$$
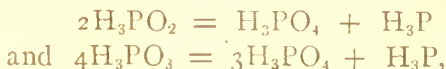
whilst orthophosphoric acid by the same treatment loses water, though the dehydration can by no means be carried beyond the production of metaphosphoric acid.

$$2H_3PO_4 - H_2O = H_4P_2O_7$$
$$\text{and } H_3PO_4 - H_2O = HPO_3$$
$$\text{or } H_4P_2O_7 - H_2O = 2HPO_3$$
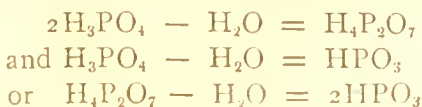
By boiling either of these products with water the ortho-acid is regenerated.

Metaphosphoric acid is convertible, by the action of heat, into several polymeric acids, $H_n P_n O_{3n}$.

Phosphorus is closely connected with the semi-metals vanadium and arsenic, by reason of the very general isomorphism of the phosphates with the arsenates and vanadates. This relationship will be adverted to in a subsequent chapter.

CHAPTER XXII.

DIVISION II.—METALLOIDS.

THE name *metalloid* obviously belongs to bodies which have the form or appearance of a metal, or which in some way resemble a metal. Hence the impropriety of applying this term, as is not uncommonly done, to such elements as the halogens, to nitrogen or phosphorus. The name is in- tended in this volume to designate a body which, although resembling a metal in most characteristics, yet lacks some one or more of the features which true metals generally present. It applies to a somewhat miscellaneous set of bodies. The question of the propriety of including hydrogen amongst them will be discussed presently, but, leaving this one element out of consideration, the test by which the sub-metallic character of most of them may be detected is the formation of more or less definite oxisalts. Their oxides are for the most part well-marked anhydric acids, but each of them is capable of producing at least one oxide which possesses basic tendencies more or less pronounced. Still putting hydrogen aside, the metalloids are comparatively imperfect conductors of heat and electricity, and generally brittle. Tin is, however, both malleable and moderately ductile.

METALLOIDS.—I. HYDROGEN.

Hydrogen is isolated from all other known bodies by reason of its extreme lightness : its specific gravity being only ·0693 when air is 1. Chemically it differs from all the non-metals in manifesting no tendency to combine with metals ; only one such compound, cuprous hydride, Cu_2H_2, being known. On the other hand hydrogen is, of all the elements, most ready to lend itself to that peculiar state of mechanical combination with metals known as " occlusion " (Chap. V., p. 31.) Palladium, for example, absorbs hydrogen largely, and the charged metal is indistinguishable in appearance from pure palladium, though its conducting power is slightly diminished. This body was regarded by Graham, who discovered it, as the realisation of the long-cherished idea of the essentially metallic character of hydrogen. But its title to recognition as a metal or metalloid is based more securely upon the resemblance which acids or hydrogen salts bear to metallic salts. In spite of a considerable number of gaseous and liquid exceptions, the majority of known acids are crystallisable bodies, often combining with water of crystallisation, and utterly indistinguishable to all appearance from ordinary saline compounds. Among common acids, for example, the following are crystallisable :—

Sulphuric acid	H_2SO_4 (below $- 35°$).
Glacial sulphuric acid	H_4SO_5 (below $9°$.)
Phosphoric acid	H_3PO_4.
Boracic acid	H_3BO_3.
Oxalic acid	$H_2C_2O_4 + 2H_2O$.
Formic acid	$HCHO_2$ (below $1°$).
Acetic acid	$HC_2H_3O_2$ (below $17°$).
Tartaric acid	$H_2C_4H_4O_6$.
Citric acid	$H_3C_6H_5O_7 + H_2O$.
Gallic acid	$HC_7H_5O_5 + H_2O$.

But the resemblance between hydrogen salts and metallic salts is not limited to external form.   They agree in chemical reactions.   When an acid is acted upon by a metal, and hydrogen is expelled, the metathesis is entirely comparable with the exchange of a more positive for a less positive metal of the ordinary recognised class.   For example, zinc decomposes hydrogen sulphate just as it decomposes copper sulphate ; in each case the less positive metal is displaced, and a new salt formed.

$$\begin{cases} H_2SO_4 + Zn = H_2 + ZnSO_4. \\ CuSO_4 + Zn = Cu + ZnSO_4. \end{cases}$$
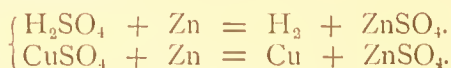
Again water, that is, hydrogen oxide or hydrate, H_2O or $H(HO)$, not unfrequently imitates metallic oxides or hydrates in their chemical reactions.   In order to produce exactly the same effect in any given case, it is only necessary to use the water in larger quantity or at a higher temperature.

The following are examples of this mode of action :—

$$\begin{cases} MgCl_2 + HgO &=& MgO &+& HgCl_2. \\ MgCl_2 + H_2O &=& MgO &+& 2HCl. \end{cases}$$

$$\begin{cases} Fe_2Cl_6 + 6NaHO = Fe_2(HO)_6 + 6NaCl. \\ Fe_2Cl_6 + 6HHO = Fe_2(HO)_6 + 6HCl. \end{cases}$$

$$\begin{cases} (C_3H_5)'''\overline{St_3}^{1} + 3NaHO = C_3H_5(HO)_3 + 3Na\overline{St}. \\ \quad \text{Stearine.} \qquad\qquad\qquad \text{Glycerine.} \qquad \text{Sodium} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{Stearate} \\ (C_3H_5)'''\overline{St_3} + 3HHO = C_3H_5(HO)_3 + 3H\overline{St}. \\ \quad \text{Stearine.} \qquad\qquad\qquad \text{Glycerine.} \quad \text{Hydrogen stearate} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{or stearic acid.} \end{cases}$$
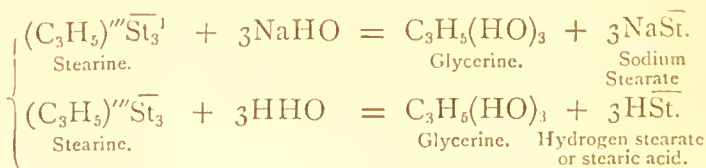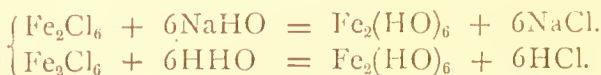
Water and acids also undergo electrolysis in the same manner as metallic salts, *e.g.*,

$$^1 \overline{St} = C_{18}H_{35}O_2.$$

$$\begin{cases} 2HHO & = & H_2 & + & (HO)_2{}^* \\ 2HCl & = & H_2 & + & Cl_2. \\ CuCl_2 & = & Cu & + & Cl_2. \end{cases}$$
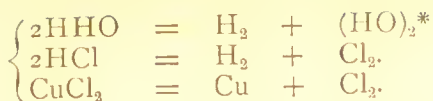
Lastly, it might be pointed out that the sour taste of hydrogen salts and their reddening effect upon vegetable blues are no more to be regarded as indications of peculiar constitution than is the alkaline reaction of many normal metallic salts or the neutrality of others. In such a series as the following we see a gradual transition from strongly alkaline to strongly acid properties.

Na_3PO_4	Na_2HPO_4	NaH_2PO_4	H_3PO_4
Very alkaline.	Alkaline.	Acid.	Very acid.
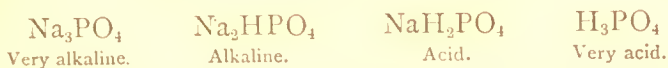
Enough has been said to indicate to the student that, despite many peculiarities which are in all probability connected with its remarkable physical characters, hydrogen displays, from a chemical point of view, features bearing an unmistakeable metallic impress.

METALLOIDS.—2. TELLURIUM.

Tellurium in many respects closely imitates sulphur and selenion. Thus it forms a gaseous telluretted hydrogen, H_2Te, the representative of hydrogen sulphide, also oxides TeO_2 and TeO_3, and acids H_2TeO_3 and H_2TeO_4 corresponding respectively with sulphur dioxide and trioxide, and with sulphurous and sulphuric acids. But tellurium is decidedly metallic in appearance, is thrown down from solution in the form of sulphide by sulphuretted hydrogen, and its lower oxide saturates acids forming salts, of which the sulphate $Te(SO_4)_2$ and nitrate $Te(NO_3)_4$ are sufficient examples.

* This has lately been shown to be the first phase in the electrolytic decomposition of water, the oxygen which is evolved being due to a secondary reaction, thus,

$$2HHO = H_2 + (HO)_2 = H_2 + H_2O + O.$$
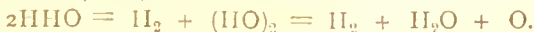
METALLOIDS.—3. TIN, TITANIUM, ZIRCONIUM.

Save for the distinctly metallic character of elemental tin and production by both tin and titanium of an inferior diadic class of derivatives, these elements bear a strong family resemblance to silicon. That the metallic function is more or less distinctly developed in them, whilst it is altogether imperceptible in silicon, is also evidenced by the existence of various oxysalts, sulphates, phosphates, etc., of tin, titanium, and zirconium, similar compounds of silicon being entirely unknown.

The most characteristic compounds of these elements are the chlorides, oxides, and acids in which they play the part of tetrads. The following are some examples compared with corresponding silicon compounds.

Silicon $S = 28$.	Tin $Sn = 118$.	Titanium $Ti = 50$	Zirconium $Zr = 89.5$.
$SiCl_4$ liquid, B.P. $50°$	$SnCl_4$ liquid, B.P. $120°$	$TiCl_4$ liquid, B.P. $135°$	$ZrCl_4$ volatile solid
SiF_4 liquefiable gas	SnF_4 fuming liquid ?	TiF_4 fuming liquid	ZrF_4 solid
M'_2SiF_6 Fluosilicates	M'_2SnF_6 Fluostannates	M'_2TiF_6 Fluotitanates	M'_2ZrF_6 Fluozirconates
Corresponding salts isomorphous.			
SiO_2	SnO_2	TiO_2	ZrO_2
	isomorphous		
	in tinstone.	in rutile.	artificial.

Atomicity of Tin and Allied Elements.

As already mentioned, tin forms, in addition to the well-defined tetrad compounds, some of which are represented in the foregoing table, an oxide, Sn_nO_n, a chloride, Sn_nCl_{2n}, a sulphide, Sn_nS_n, and some other compounds in which it seems to be diad. In the absence of direct

evidence in favour of the one view or the other, it is customary to represent the oxide as SnO, and the chloride as $SnCl_2$. In favour of the formula SnO, we have its analogy to that of carbonic oxide, CO, though there is absolutely no resemblance in the properties of the two bodies to support such a view.

For stannous chloride representing it as a dichloride we have no example among the compounds of carbon and silicon. On the whole, it seems, therefore, probable that the tin retains its quadrivalence in both the oxide and the chloride, and their formulæ in accordance with this view would be written thus :—

$$Sn_2Cl_4 \quad \text{or} \quad Cl_2 = Sn = Sn = Cl_2$$
$$Sn_2O_2 \quad \text{or} \quad O = Sn = Sn = O.$$
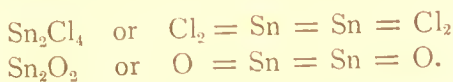
METALLOIDS.—4. VANADIUM, ARSENIC, ANTIMONY, BISMUTH. (For numerical relations of atomic weights see *Non-metals*, *Class* 5, p. 193.)

These elements are all quinquivalent in their most advanced states of combination, the tendency to assume this condition being the least prominent in the case of bismuth, which is of the whole class the most decidedly metallic.

Vanadium is remarkable for the extensive series of oxides, chlorides, and oxychlorides to which it gives rise, the different stages of oxidation of its dissolved compounds being characterised by a strange variety of colour, a yellow or red tint belonging to the higher, and a blue or green tint especially to the lower oxides, which thus resemble some of the compounds of chromium, molybdenum, and tungsten. Oxides of phosphorus, arsenic, antimony, and bismuth, except Bi_2O_5, are white.

The known oxides of vanadium have the formulæ V_2O, VO or V_2O_2, V_2O_3, VO_2 or V_2O_4, and V_2O_5, thus running parallel with the series of nitrogen oxides. There are three

chlorides, VCl_2 or V_2Cl_4, VCl_3 and VCl_4. The last is a brown liquid boiling at $154°$ and yielding a vapour of density $96·5$, which is half the molecular weight represented by the formula VCl_4. Vanadium, therefore, does not maintain the usual persistence of odd or even atomicity throughout its combinations (see Chap. XIX).

The vanadates M'_3VO_4 are isomorphous with the phosphates M'_3PO_4. Metavanadates and pyrovanadates also exist corresponding with meta- and pyrophosphates, besides a certain number of anhydro-meta-salts $M''(VO_3)_2.V_2O_5$ and $M''(VO_3)_2.2V_2O_5$.

The analogies of arsenic, antimony, and bismuth will be most satisfactorily brought out by tabulating the formulæ of their leading compounds. For the sake of comparison, the corresponding compounds of phosphorus are placed side by side with them.

The vapour densities of phosphorus and arsenic lead to the molecular formulæ P_4 and As_4 for those elements; but antimony and bismuth, though easily fusible metals, are not volatile enough to give vapour at any manageable temperature. Their molecular formulæ are therefore unknown.

Phosphorus	Arsenic	Antimony	Bismuth
Hydrides and Ethylides.			
PH_3 $P(C_2H_5)_3$	AsH_3 $As(C_2H_5)_3$	SbH_3 $Sb(C_2H_5)_3$	— $Bi(C_2H_5)_3$
Chlorides.			
PCl_3 PCl_5	$AsCl_3$ —	$SbCl_3$ $SbCl_5$	$BiCl_3$ —
Oxides.			
P_2O_3 P_2O_5	$(As_2O_3)_2$ As_2O_5	Sb_2O_3 Sb_2O_4 Sb_2O_5	Bi_2O_3 Bi_2O_4 Bi_2O_5

Phosphorus.	Arsenic.	Antimony.	Bismuth.
		Acids.	
HPH_2O_2	$\overline{HAsO_2}$?	$\overline{HSbO_2}$	$\overline{HBiO_2}$
H_2PHO_3	H_3AsO_3	--	$HBiO_3$
HPO_3	$HAsO_3$	$HSbO_3$	
H_3PO_4	H_3AsO_4	H_3SbO_4?	
$H_4P_2O^7$	$H_4As_2O_7$	$H_4Sb_2O_7$	
		Sulphides.	
P_2S	As_2S_2		Bi_2S_2
P_2S_3	As_2S_3	Sb_2S_3	Bi_2S_3
P_2S_5	As_2S_5	Sb_2S_5	

A few peculiarities exhibited by particular compounds occurring in this table demand notice.

1. The faculty of neutralising acids possessed in so remarkable a manner by ammonia is displayed by phosphoretted hydrogen towards one acid only, hydriodic acid, and altogether vanishes in the arsenic and antimony hydrides.

2. The ethylated and corresponding methylated compounds are characterised not so much by a power of combining with acids, as by a tendency to unite with O, S, Cl_2, I_2, &c., whereby the central element is brought to a state of saturation.

3. No pentachloride, pentabromide or oxychloride, or bromide of arsenic is known.

4. The vapour density of arsenious oxide (white arsenic) is 198. Hence its molecular weight is $198 \times 2 = 396$ and formula As_4O_6. It is usual to represent the oxides of phosphorus by the formulæ written in the table ; but if the trioxide could be obtained in a pure state and its vapour density determined, it is by no means improbable that its molecular formula would also be doubled.

White arsenic occurs in commerce in the form of white masses with conchoidal fracture, often exhibiting a banded appearance, due to the presence of the isomeric vitreous

and porcellanous varieties. The former is converted into
the latter by pulverisation or by protracted boiling with
water. Either variety is but slightly soluble in water, and
the solution gives only a feebly acid reaction. Porcellanous
arsenic probably owes its opacity to crystalline structure.
By careful sublimation at regulated temperatures white
arsenic may be obtained either in the form of trans-
parent regular octahedra or in prismatic crystals of the
trimetric system. It is, therefore, isodimorphous with
antimonious oxide.

White arsenic is a feebly basic, as well as acid, an-
hydride. Its best known salt is the double tartrate
$K(AsO)C_4H_4O_6$, which is analogous to the potassio-tartrates
of antimony, $K(SbO)C_4H_4O_6$ (tartar-emetic), and boron
$K(BO)C_4H_4O_6$.

5. Phosphoric oxide is volatile and stable, but As_2O_5,
Sb_2O_5, Bi_2O_5, are resolved by heat into oxygen and a lower
oxide.

6. Arsenious acid appears to be normally tribasic, the
yellow silver salt containing Ag_3AsO_3. It therefore
differs from phosphorous acid, which is dibasic.

Phosphorous Acid.   Arsenious Acid.

$$O = P \overset{\displaystyle OH}{\underset{\displaystyle H}{\diagup}} OH \qquad As \overset{\displaystyle OH}{\underset{\displaystyle OH}{\diagup}} OH$$
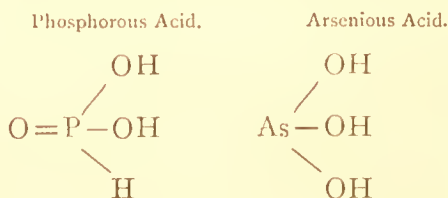
7. The orthophosphates and arsenates correspond in
every respect with each other, and in many cases with the
orthovanadates. In addition to the ordinary salts of the
common phosphate type, $M'H_2PO_4$, M'_2HPO_4 and M'_3PO_4,
there is a remarkable series of compounds occurring as
minerals in combination with a chloride or fluoride.

Apatite	$3[Ca_3(PO_4)_2]$. CaF_2 or $Ca_5(PO_4)_3F$
or	$3[Ca_3(PO_4)_2]$. $CaCl_2$ or $Ca_5(PO_4)_3Cl$
Pyromorphite	$3[Pb_3(PO_4)_2]$. $PbCl_2$ or $Pb_5(PO_4)_3Cl$
Mimetine	$3[Pb_3(AsO_4)_2]$. $PbCl_2$ or $Pb_5(AsO_4)_3Cl$
Vanadite	$3[Pb_3(VO_4)_2]$. $PbCl_2$ or $Pb_5(VO_4)_3Cl$.

Orthoantimonates and orthobismuthates are unknown, unless we consider the intermediate tetroxides in that light : antimonious orthoantimonate Sb_2O_4 or $Sb'''(Sb^vO_4)$ and bismuthous orthobismuthate Bi_2O_4 or $Bi'''(Bi^vO_4)$. Several orthosulphantimonates are, however, known ; the sodium salt, for example, $Na_3SbS_4.9H_2O$, crystallising readily.

8. The sulphides of arsenic, antimony, and bismuth act as sulphur anhydrides, and in combination with the sulphides of silver, lead, copper, and other metals, constitute several interesting minerals.

METALLOIDS.—5. NIOBIUM, TANTALUM.

These two rare metals may be regarded as about equally related on the one hand to tetrad tin and its allies, and on the other to hexad molybdenum and tungsten. With the latter elements, indeed, there is not only considerable analogy of properties, but a curious coincidence of atomic weights.

$$Mo^{VI}\ 96 \qquad Nb^v\ \ 94$$
$$W^{VI}\ 184 \qquad Ta^v\ 182$$

Niobium and tantalum are pentad elements, and are characterised by the production of pentachlorides in the form of yellow, fusible, volatile bodies, the vapour densities of which accord with the formulæ $NbCl_5$ and $TaCl_5$ respectively.

The metals themselves are only known in the condition of black powders, which resist the attacks of most acids, except hydrofluoric acid, in which they are slowly soluble with evolution of hydrogen. Their fluorides unite with the fluorides of the alkali-metals, forming soluble and crys-

tallisable double salts, $2KF,NbF_5$ and $2KF,TaF_5$.   But niobium, at least, is also specially characterised by the production of oxyfluorides, which, in combination with the fluorides of the more positive metals form salts which are isomorphous with the fluotitanates, fluostannates, fluotungstates, and fluozirconates.   The following pairs of compounds, for example, crystallise in the same form :—

$$3KF . HF . NbOF_3$$
$$3KF . HF . SnF_4$$

$$2NH_4F . NbOF_3$$
$$2NH_4F . WO_2F_2$$

$$3NH_4F . NbOF_3$$
$$3NH_4F . ZrF_4.$$

$$2NH_4F . CuWO_2F_4$$
$$2NH_4F . Cu\ TiF_6.$$
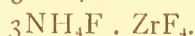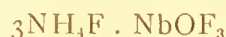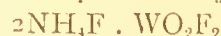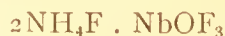
It thus appears that groups of elements of different atomicities may occasionally replace one another isomorphously, provided the valency or atomicity of the various groups is the same.

The radicles which are thus at the same time chemically and isomorphously equivalent to one another in the foregoing compounds are as follows :—

$(TiF_2)''$, $(ZrF_2)''$, $(SnF_2)''$, $(NbOF)''$, and $(WO_2)''$.
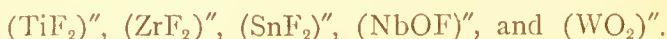
Such relations are of precisely the same character as are those of the group $(NH_4)'$, ammonium, to the single metallic atom K', and precisely the same conclusions, neither more nor less, can be deduced from them.

METALLOIDS. 6.

Molybdenum	$Mo = 96$
Tungsten	$W = 184$
Uranium	$U = 240.$
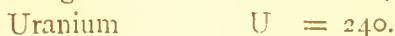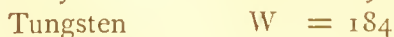
These elements are heavy metallic bodies : tungsten and uranium being especially distinguished both by high atomic weight and specific gravity.

They appear to be hexads, though, of the three, tungsten alone produces a hexchloride, and that unstable. In the formation of trioxides and volatile dioxydichlorides (general formula $M^{VI}O_2Cl_2$) they resemble chromium, but they differ from that metal in furnishing neither sesquioxide nor monoxide analogous to Cr_2O_3 and CrO.

The infraction of the law of even numbers occurring in the case of the chlorides and bromides of tungsten, and in the chlorides of uranium, has been already adverted to (Chap. XIX). Molybdenum, like the rest, seems to form a pentachloride.

The trioxides, MoO_3, WO_3, and UO_3, are generally acid anhydrides. Some of the tungstates of the form M'_2WO_4 seem to be isomorphous with the corresponding chromates and sulphates, but the majority are extremely complex.

These trioxides also exhibit a feebly basic function, the oxysalts of uranium being the most stable. The nitrate, for example, a yellow crystallisable salt, has the formula $(UO_2)''(NO_3)_2.6H_2O$, and the sulphate and oxalate are formed upon the same type.

Molybdenum and tungsten agree in forming trisulphides, MoS_3 and WS_3, which are unrepresented among the compounds of uranium and of chromium.

CHAPTER XXIII.

DIVISION III.—METALS.

The following are the principal characteristics of the metals as a class :—

1. Metals are all solids at the temperature of the air, with the sole exception of mercury, which is ordinarily liquid, but solidifies at − 40°. The solid metals differ very much in their fusibility, the metals of the alkalis melting most readily (potassium at 62°·5), whilst platinum and its congeners require the highest temperature of the oxyhydrogen flame.

2. Metals combine great opacity with high reflective power, exhibiting the appearance which is sufficiently well known as metallic lustre. Gold in very thin leaves transmits a greenish light.

3. That all the common metals are heavy is a fact familiar to everyone ; but an inspection of the table of specific gravities given at the commencement of the section will lead to the conclusion that there are many which are much lighter than the familiar iron, copper, lead, and silver, whilst there are several which are even heavier than gold. As a curious fact, the heaviest solid known is a metal, platinum (sp. gr. 21·5), and the lightest known *solid* is also a metal, namely, lithium, whose specific gravity is only ·578.

But it is of much greater importance to observe that in many cases groups of metals which are associated together by reason of community of chemical properties, have also specific gravities which nearly approximate to one another.

As examples of this may be cited the alkali metals, lithium, potassium, · sodium, rubidium ; the alkaline earth metals, magnesium, calcium, strontium, barium ; the metals of the iron family, chromium, iron, manganese, nickel, cobalt,

and copper ; silver, lead, and thallium ; and lastly, the noble metals, gold, iridium, and platinum. Possibly other similar associations might be discovered, but for the fact that several metals are scarcely known in a compact form, and in other cases the numbers may be more or less incorrect in consequence of the presence of impurity in the specimens operated upon.

4. Metals are the best conductors of heat. They differ widely among themselves in this respect, as the following rough comparison shows. Silver, as the best conductor, is placed at the head of the list. The numbers may be taken to represent the relative lengths of bars of equal diameter which, by applying a common source of heat to one extremity, would become equally heated in the same time.

Silver	1000
Copper	736
Gold	532
Iron	119
Lead	85
Platinum	84
Bismuth (an imperfect metal) .	18

5. Metals are the best conductors of electricity. The metals given in the foregoing list stand in nearly the same order as regards electric conductivity.

6. Metals are almost always malleable, though in a few cases this happens only at slightly elevated temperatures. Frozen mercury is malleable.

7. Many metals are ductile. It by no means follows, however, that malleability and ductility should be manifested in the same degree by a given metal. Gold, for example, is by far the most malleable metal, though in point of ductility it is surpassed by platinum.

8. The oxides of metals are very generally basic.

The basigenic character belongs exclusively to the metals and metalloids. But the oxygenic function is discharged

almost equally well by particular elements in all three divisions.

The transition from metal to non-metal is, therefore, not accomplished by any sudden break, and the student must be prepared to encounter great, and, perhaps, insurmountable difficulties in any attempt to establish a line of demarcation between them.

The following series of oxides will serve to indicate how gradually the one character disappears as the other is developed. The symbols in black type represent basic oxides, those in Roman represent oxides which go to the negative side of the salts into which they enter.

From Non-metallic to Metallic.

SO_3 WO_3 CrO_3 FeO_3
SO_2 WO_2

$\quad\quad\quad Cr_2O_3$ Fe_2O_3 Ni_2O_3
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ No Salts

$\quad\quad\quad CrO$ FeO NiO CuO
$\quad\quad\quad$ Extremely
$\quad\quad\quad$ oxidisable.

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Cu_2O$ Ag_2O K_2O
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ Salts unstable.
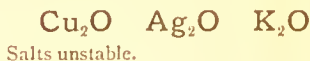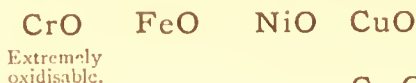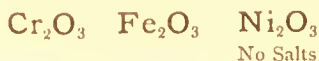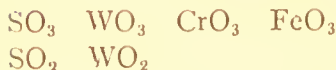
METALS.—I. THE METALS OF THE ALKALIS. MONADS.

Lithium Li $=$ 7 $\left.\begin{array}{l}\\ \\ \\ \end{array}\right\}$ $\dfrac{Li + K}{2} = 23$
Sodium Na $=$ 23
Potassium K $=$ 39·1

Potassium K $=$ 39·1 $\left.\begin{array}{l}\\ \\ \\ \end{array}\right\}$ $\dfrac{K + Cs}{2} = 86$
Rubidium Rb $=$ 85·4
Cœsium   Cs $=$ 143
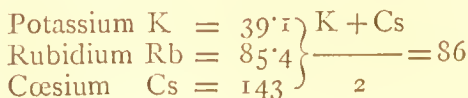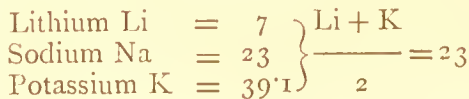
Salt Type, M′Cl.

These are soft, white, light, easily fusible, and somewhat volatile metals. They oxidise rapidly in the air, but differ

materially from one another in this respect, their affinity for oxygen increasing with the atomic weight. This is shown especially by the spontaneous inflammability of rubidium, and the impossibility of obtaining cœsium by decomposition of its carbonate with charcoal. They all decompose cold water with formation of a soluble hydrate and evolution of hydrogen gas. But as a consequence of the inferior energy of lithium and sodium, the heat developed by their action upon water is not sufficient to cause the ignition of the escaping hydrogen, whereas the hydrogen disengaged by potassium inflames instantly, and continues to burn with a purple light, due to the accompanying vapour of the metal.

The hydrates of these metals are all fusible, scarcely decomposed by heat, but volatilising at high temperatures, very soluble in water, and the solutions caustic to the skin, alkaline to litmus, and absorbing carbonic acid from the air. The hydrates also saponify oils and fats, and the resulting soaps are alkaline and soluble.

The chlorides, sulphides, sulphates, phosphates, and carbonates of the alkali metals are all soluble in water, and their chlorides and sulphates yield perfectly neutral solutions. The sulphates combine with the sulphate of aluminium and the allied metals, generating highly characteristic double salts, called " alums," which crystallise in octahedra. A crystallised lithium-alum has not yet been described, but this is probably owing to its great solubility.

The alkali salts all communicate intense and characteristic colours to the Bunsen flame, and the spectrum (p. 41) of the light so produced exhibits in each case a comparatively small number of bright lines.

As indicated by the atomic weights, the alkali-metals may be divided into two sub-groups. In the one we have potassium, cœsium, and rubidium, which are distinguished by greater chemical activity and inferior solubility of

their salts, notably of the platinochlorides and acid tartrates.

$$K_2PtCl_6 \qquad KHC_4H_4O_6$$
$$Rb_2PtCl_6 \qquad RbHC_4H_4O_6$$
$$Cs_2PtCl_6 \qquad CsHC_4H_4O_6$$

Sodium and lithium, though entirely comparable with potassium, are yet distinguished from it by much feebler chemical energies, by the solubility of their platino-chlorides, acid tartrates, and alums, and by different minor peculiarities. Sulphate of sodium, for example, crystallises with ten molecules of water, whilst sulphate of potassium is anhydrous. The carbonates also differ, that of sodium forming large efflorescent crystals containing $10H_2O$, the carbonate of potassium occurring in small deliquescent granules, containing usually about one or two molecules of water.

Both sodium and potassium yield unstable peroxides, Na_2O_2 and K_2O_2, and potassium is even capable of passing to a higher stage of oxidation, the product being a tetroxide, K_2O_4. No salts corresponding with these oxides exist.

METALS.—2. METALS OF THE ALKALINE EARTHS.   DIADS.

$$\left. \begin{array}{ll} \text{Calcium} & Ca = 40 \\ \text{Strontium} & Sr = 87\cdot5 \\ \text{Barium} & Ba = 133 \end{array} \right\} \frac{Ca + Ba}{2} = 88\cdot5$$
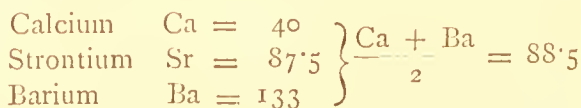
Salt Type, $M''Cl_2$.

These three metals, obtained by the electrolysis of their fused chlorides, are yellowish, hard, and fusible, and extremely oxidisable. They are, however, less oxidisable than the metals of the alkalis, though they are still capable of decomposing cold water. They also communicate characteristic colours to flame, and yield spectra (p. 41) which are easily recognisable but somewhat more complex than those of the alkalis generally.

The hydrates of the alkaline earths are white substances

which are decomposed by heat into water and the anhydrous oxides. They are far less soluble in water than the alkalis, and are proportionately less caustic, alkaline, and attractive of carbonic acid. They saponify fats, but the resulting soaps are generally insoluble in water.

The salts of barium, strontium, and calcium are, as a rule, perfectly neutral.

The chlorides and sulphides are soluble in water, but the sulphates, phosphates, and carbonates are insoluble.

Oxide of barium or baryta exposed to a current of air or oxygen at a heat short of redness, absorbs oxygen and becomes converted into a peroxide, BaO_2. The corresponding peroxides of strontium and calcium are obtained as white precipitates by adding solution of hydric peroxide to lime or strontia water. All three are resolved by ignition into oxygen gas, and a residue of the protoxide. They are also soluble in hydrochloric acid, yielding peroxide of hydrogen and the chloride of the metal, *e.g.*,

$$BaO_2 + 2HCl = BaCl_2 + O_2H_2.$$

Hence it is presumable that they have the same constitution as hydric peroxide, the oxygen atoms partly satisfying each other's attractions, according to the following graphic formulæ :—

Hydric peroxide.
$$H—O$$
$$|$$
$$H—O$$

Baric peroxide.
$$Ba'' \diagdown\diagup \begin{matrix} O \\ | \\ O \end{matrix}$$
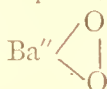
Of the three elements, barium, with the highest atomic weight, is decidedly most basylous. Strontium standing next is, in respect to some characters, more nearly related to barium than to the third member of the series, calcium. Thus the nitrates of strontium and barium crystallise in anhydrous octahedra, isomorphous with lead nitrate, $Pb(NO_3)_2$. The sulphates of these two metals are also anhydrous, and are practically insoluble in water and acids.

Nitrate of calcium is a deliquescent salt, soluble in alcohol and crystallising in prisms, which contain $Ca(NO_3)_2.4H_2O$. Its sulphate, in the form of gypsum, combines with two molecules of water, is perceptibly soluble in water, and much more freely so in hydrochloric acid.

On the other hand, strontium agrees with calcium in the production of a deliquescent chloride, which is soluble in alcohol, whilst the barium chloride is insoluble in alcohol.

The crystallised chlorides have the following formulæ :—

Chloride of Calcium	$CaCl_2 \cdot 6H_2O$
,, Strontium	$SrCl_2 \cdot 6H_2O$
,, Barium	$BaCl_2 \cdot 2H_2O$

METALS.—3. ZINC GROUP. DIADS.

$$\left. \begin{array}{lll} \text{Magnesium} & Mg = & 24 \\ \text{Zinc} \quad - & Zn = & 65 \\ \text{Cadmium} & Cd = & 112 \end{array} \right\} \frac{Mg + Cd}{2} = 68.$$

Salt Type, $M''Cl_2$.

These elements are rightly associated together in consequence of a very obvious seriation of properties, notwithstanding that they are far less intimately related to one another than, for example, the metals of the alkaline-earth family. Magnesium is a white metal, zinc and cadmium faintly bluish-white, and all three are volatile. Their volatility somewhat strangely increases in proportion as the atomic weight increases, whilst their basigenic power diminishes. That zinc is decidedly more positive than cadmium is shown by its power of precipitating cadmium in the metallic state from its solutions. That magnesium is more positive than the other two is shown by its power of decomposing water when heated with it, or more readily if previously coated with pulverulent copper.* Also by the precipitation

* Zinc and cadmium, when coated with spongy copper, are also capable of decomposing water slowly.

of both zinc and cadmium when metallic magnesium is introduced into solutions of their salts.

Magnesium, zinc, and cadmium are all easily combustible in air or oxygen, the combustion of the former two being attended by the emission of a dazzling light.   Each metal forms one oxide : MgO, a white unalterable powder ; ZnO, a white powder, becoming yellow when heated ; CdO, a yellowish-brown powder.   These oxides are insoluble in water, that of magnesium only showing a faint alkaline reaction when placed upon wet test paper.   The oxides and hydrates are readily soluble in solutions of ammoniacal salts.

The hydrates are easily resolved, by being heated, into water and the oxide, and the carbonates in like manner give up carbonic anhydride, leaving a residue of the oxide.

The chlorides are volatile, deliquescent solids.

The sulphide of magnesium is an earthy substance which is decomposed even by water.

$$MgS + 2OH_2 = Mg(OH)_2 + SH_2$$
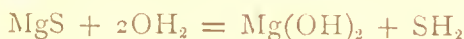
and is therefore not precipitated on the addition of a soluble sulphide to a magnesian solution.

Zinc sulphide (native = blende) is a white precipitate easily soluble in diluted mineral acids, and hence only imperfectly precipitated by the action of hydrogen sulphide upon the solution of a zinc salt.

Cadmium sulphide (native = greenockite) is a yellow precipitate thrown down by hydrogen sulphide from acidified solutions of cadmium salts.

The sulphates of these metals are, perhaps, the most characteristic of their salts.   They are soluble in water, and have the following formulæ :—

Magnesium sulphate $MgSO_4.7H_2O$
Zinc sulphate   . $ZnSO_4.7H_2O$
Cadmium sulphate . $CdSO_4.4H_2O$

The magnesium and zinc salts crystallise in four-sided

prisms, isomorphous with the corresponding nickel sulphate.

All three combine with potassium sulphate, generating double salts, which crystallise with six molecules of water :

$$MgSO_4 \ . \ K_2SO_4 \ . \ 6H_2O$$
$$ZnSO_4 \ . \ K_2SO_4 \ . \ 6H_2O$$
$$CdSO_4 \ . \ K_2SO_4 \ . \ 6H_2O$$
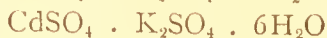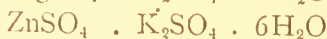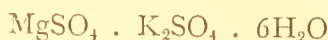
Sulphates isomorphous with these are produced by several other metals, such as copper and iron, and will be referred to in the proper place.

A general review of its properties indicates that magnesium forms a connecting link between zinc and calcium. From the latter it differs chiefly in the insolubility of its hydrate in water, and the solubility of the same compound in ammonium chloride. Sulphate of magnesium is also distinguished from sulphate of calcium by its ready solubility.

<div align="center">METALS. 4.</div>

Silver $Ag = 108$.	Mercury $Hg = 200$
Salt type, $M'Cl$.	*Salt types, M''_2Cl_2,*
	and $M''Cl_2$.

Silver is a white metal, very malleable and ductile, fusible at a red heat, and volatilising in blue vapour at very high temperatures. It is the best known conductor of heat and electricity. The only known monad metal beside the metals of the alkalis, it is undoubtedly related to them, for its sulphate is isomorphous with anhydrous sodium sulphate, and by combination with aluminium sulphate it yields a true alum crystallising in octahedra. In almost every other respect, however, it differs from them.

Thus its specific gravity is high, $10 \cdot 5$, and it is quite untarnished by pure air, whether dry or moist, the blackening so often observed being due to the formation of a film of sulphide. Pure silver has the singular property of occluding.

when fused in the air, a considerable volume of oxygen, which escapes as the temperature goes down and the metal solidifies. Silver has no action upon water or steam at any temperature, and is quickly reduced from its salts by zinc, iron, or even mercury. The oxide is said to be sufficiently soluble in water to give a faintly alkaline reaction, but it differs entirely from potash or soda in appearance and in its decomposability by heat. The chloride, iodide, sulphide, carbonate and phosphate of silver are all insoluble in water, and the sulphate very sparingly soluble.

Silver forms a peroxide, Ag_2O_2, even less stable than the potassium peroxide. There is also a suboxide, Ag_4O, the composition of which is, however, not very well established.

The relations of silver to the alkali-metals on the one hand, and to mercury on the other, are about equally distant. This connection is obscurely indicated by comparison of their atomic weights, from which it may be seen that silver is intermediate between sodium and mercury.

$$\frac{Na\ 23\ +\ Hg\ 200}{2} = 111\cdot5\ (Ag = 108).$$

Mercury, like silver, is a white metal, crystallising in the regular system and volatilising, though much more readily. Both are easily reducible to the metallic state, and the metals are both incapable of decomposing water or hydrochloric acid. Mercury, however, is slowly oxidised by heating in air or oxygen. Both are soluble in nitric acid, and when boiled with concentrated sulphuric acid sulphur dioxide is in each case evolved, and a sulphate produced in the form of a sparingly soluble crystalline powder.

Silver oxide, Ag_2O, and mercurous oxide, Hg_2O, are both nearly black, insoluble in water, and resolved by heat into oxygen gas and the metal.

Silver chloride, AgCl, and mercurous chloride, Hg_2Cl_2, are both obtainable by precipitation as white powders, which

blacken, the silver salt quickly, the mercury salt slowly, on exposure to light.

The iodides are both yellow and insoluble. The chief distinction between silver and mercurous salts lies in the volatility of the latter.

As regards the formulæ of the mercurous compounds, their analogy to the compounds of silver points to the adoption of similar formulæ.

$$Ag - O - Ag. \qquad Hg - O - Hg.$$
$$Ag - Cl, \text{ etc.} \qquad Hg - Cl, \text{ etc.}$$
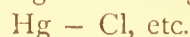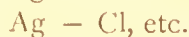
But, inasmuch as the low vapour-density of calomel, $117.75 = \dfrac{200 + 35.5}{2}$, has been traced to dissociation (Chap. XVII.), this, and consequently all other mercurous compounds, must be represented as containing diad mercury, thus :

$$Hg_2O \quad = \quad \begin{matrix} Hg \\ | \\ Hg \end{matrix} \Big\rangle O$$

$$Hg_2Cl_2 \quad = \quad \begin{matrix} Hg-Cl \\ | \\ Hg-Cl \end{matrix}$$
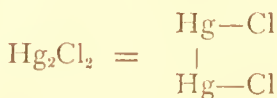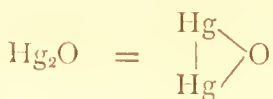
The mercuric salts, in which the mercuric atom exercises its full combining capacity, are almost without parallel as regards properties among metallic salts. Their formulæ are written upon the same type as those of the salts of cadmium and zinc, but it cannot be said that the resemblance extends much farther.

In one respect, however, metallic mercury agrees with the metals cadmium and zinc. Notwithstanding its much greater volatility, its vapour density, like that of the other two, is the half of its atomic weight. Hence, whilst the molecules of all other volatile elements are polyatomic,

those of the three metals referred to are simply monatomic, the atom and the molecule being represented in each case by one and the same symbol or formula,—Zn, Cd, Hg.

The following are the most important mercuric compounds. All are volatilisable.

Oxide. HgO. A red or yellow powder darkening by heat, and decomposed below redness into Hg and O_2.

Chloride. $HgCl_2$. White, crystallisable, soluble in water, alcohol, and ether. Vapour density $\frac{200 + 71}{2} = 135\cdot5$.

Amidochloride. $HgNH_2Cl$. Commonly known as 'White Precipitate.' Representable either as an amidochloride,

$$Hg'' \Big\langle {\overset{'''}{N} = H_2 \atop Cl}$$
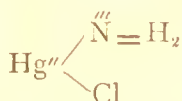
or as chloride of mercuric-ammonium,

$$\begin{array}{c} Hg \\ \diagup\!\!\diagup \\ \overset{v}{N} = H_2 \\ \diagdown \\ Cl \end{array}$$
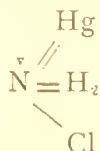
The former view is preferable, considering its formation from mercuric chloride by ammonia.

$$Hg \Big\langle {Cl \atop Cl} + {NH_2H \atop NH_3} = Hg \Big\langle {NH_2 \atop Cl} + \Big\{ {HCl \atop NH_3}$$
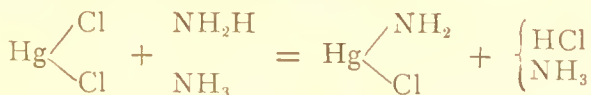
Iodide. HgI_2. Red or yellow, dimorphous, insoluble in water, soluble in ether and in solution of potassic iodide.

Sulphide, HgS. Cinnabar, dark red masses of hexagonal prisms. Artificial vermilion, bright red powder.

Sulphate. $HgSO_4$. Colourless, minute, prismatic crystals, characteristically decomposed by water with formation of yellow 'turpeth mineral,' or trimercuric orthosulphate $Hg_3O_2SO_4$ or $Hg''_3(SO_6)^{VI}$.

METALS. 5.

Indium, In $= 113\cdot4$.
Triad. Salt type, $M'''Cl_3$.

Thallium, Tl $= 204$.
Triad. Salt types $M'Cl$ and $M'''Cl_3$.

Lead, Pb $= 207$.
Tetrad. Salt type, $M''Cl_2$.

INDIUM is a very rare metal, occurring in minute quantities in zinc ores. It is white, soft, fusible, but not particularly volatile. It resists oxidation up to a temperature somewhat beyond its melting point, $176°$, but at a red heat it takes fire in the air and burns with a blue flame and brownish oxide smoke. It is readily attacked by nitric acid, but dissolves slowly in dilute hydrochloric or sulphuric acid.

Oxide of indium, In_2O_3, is a pale yellow powder, becoming darker when heated. The sulphide is an orange yellow precipitate, insoluble in acetic, but soluble in mineral, acids. Chloride of indium, $InCl_3$, is volatile at a red heat, but undergoes decomposition when heated in the air, and the solution of the chloride also leaves on evaporation an oxychloride.

The spectrum of indium is highly characteristic, consisting only of two bright blue or indigo bands.

THALLIUM was originally discovered, and occurs most abundantly in certain kinds of copper and iron pyrites. It is a very soft, nearly white metal, which tarnishes quickly but superficially in the air. It closely resembles lead in physical properties, except that it is softer and streaks paper more readily. It melts at $294°$, and volatilises at a red heat. It is capable of burning brilliantly in oxygen.

Thallium forms two classes of compounds, those in which it is univalent being the more stable.

The following are the most characteristic of *thallous* compounds :—

Chloride. TlCl. A white curdy precipitate, resembling

silver chloride, but crystallisable from boiling water, and combining with platinic chloride to form a yellow, slightly soluble, crystalline compound, Tl_2PtCl_6.

Oxide, Tl_2O, and Hydrate, $TlHO$. These compounds are soluble in water, the solution being strongly alkaline, and reacting in the same manner as caustic potash. The hydrate differs from the alkali hydrates in losing the elements of water when exposed over oil of vitriol in a vacuum. The residual oxide is almost black, and after fusion crystalline.

Sulphate. Tl_2SO_4. A soluble colourless salt, isomorphous with sulphate of potassium. It combines with aluminium sulphate, forming a true alum, $TlAl(SO_4)_2.12H_2O$.

Sulphide. Tl_2S. A brown precipitate, soluble in acids.

Thallic Compounds.

Chloride. $TlCl_3$. A soluble salt, crystallisable by evaporation of its solution in a vacuum. It melts and evolves chlorine at high temperatures. It combines with the monochloride, forming two compounds, Tl_4Cl_6 or $3TlCl . TlCl_3$, and Tl_2Cl_4 or $TlCl . TlCl_3$. It forms similar compounds with the chlorides of potassium and ammonium.

Oxide. Tl_2O_3. A dark red powder, insoluble in water, and reduced by heat to thallous oxide. Thallium is readily obtained from its salts either by electrolysis, by the action of zinc, or by fusion with cyanide of potassium.

The ordinary spectrum of thallium is the simplest known. It consists of a single bright band in the green.

LEAD is a bluish metal, so soft as to streak paper, and possessing very little tenacity. Its specific gravity is 11.36, a number very near to, and intermediate between, that of thallium, 11.9, and of silver, 10.53. The latter metal is very constantly associated with it, occurring as sulphide in, probably all, galena. Lead melts at 326°, and at a red heat volatilises freely. A freshly cut surface tarnishes rapidly in air, but oxidation, except of the melted metal, does not proceed to any appreciable extent.

Lead forms two oxides of definite composition, namely, litharge, PbO, and the peroxide, PbO_2, besides several mixed oxides containing the elements of these two in various proportions. The red oxide is generally $2PbO$, PbO_2, or Pb_3O_4. When plumbic peroxide is acted upon by hydrochloric acid, it does not, like barium peroxide, give rise to hydrogen peroxide, but to a tetrachloride, $PbCl_4$. In these two compounds, therefore, lead is quadrivalent, and their formulæ must be written as follows :—

$$O = Pb = O \qquad \begin{matrix} Cl \\ Cl \end{matrix} \!\! \diagdown \!\! Pb \!\! \diagup \!\! \begin{matrix} Cl \\ Cl \end{matrix}$$
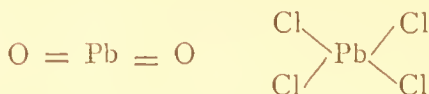
The tetrachloride is a very unstable compound, and no oxysalts corresponding with it are known.

The ordinary salts of lead are typified by the *dichloride*, $PbCl_2$, a white, sparingly soluble salt, crystallisable from boiling water.

The *oxide*, PbO, is a dull yellow, the hydrate, a white powder. Both are slightly soluble in water, the solubility, like that of lime, being increased by the addition of sugar. The solutions are strongly alkaline, and absorb carbonic acid from the air.

Sulphate, $PbSO_4$. In the form of lead-vitriol, isomorphous with heavy spar, $BaSO_4$.

Carbonate, $PbCO_3$. As white lead ore or cerusite, isomorphous with witherite, $BaCO_3$.

Nitrate, $Pb(NO_3)_2$, crystallises in octahedra, isomorphous with barium nitrate.

Sulphide. PbS. Black insoluble powder or crystallised in shining cubes (galena).

Relations of Thallium, Lead, and Indium.

The relations of thallium both to potassium and lead are exceedingly well-marked. With potassium it agrees in the alkalinity of its oxide and the characters of the platinochloride, acid tartrate, sulphate, and alum. But it differs

from potassium and resembles lead in the ready reduci-
bility of the metal, in its high atomic weight and specific
gravity, and in the characters of the sulphide, monochloride,
and other salts.

Lead, in its turn, has strong points of resemblance on the
one hand to thallium, and on the other to barium, as indi-
cated by the isomorphism of many lead and barium salts.

The relations which are thus manifested by these metals
serve to bring into view the connection which they un-
doubtedly have with other metals, the characters of which
have already been discussed. Without attempting to trace
out any further parallels of the same kind, a task which the
student can very well perform without assistance, we may
just indicate the direction in which analogies will be most
readily detected by arranging the symbols of the most
important of these metals in the following order :—

$$
\begin{array}{llll}
(Hg_2)'' \\
or \quad Hg' \text{——} Hg'' & Pb'' \text{——} Tl' \\
\quad Ag & Cd & Ba & Cs \\
\quad | & Zn & Sr & Rb \\
\quad Na & Mg \text{ — } Ca & K
\end{array}
$$
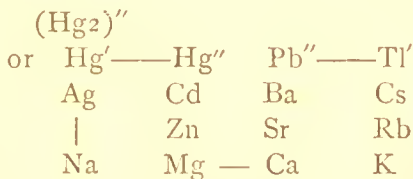
Regarding the position of indium among the metals, some
diversity of opinion exists. There appears to be little doubt
of its near approximation to cadmium, both in respect of its
atomic weight and the characters of its oxide, sulphide,
chloride, and other compounds. But in the extreme simpli-
city of its spectrum it is comparable only to some member
of the group of alkali metals, especially to sodium.

In order to indicate these relations we may range the
symbols of these metals in a series, the parallelism of which
to the thallium series will be at once apparent.

	Atc. Wt.	Sp. Grav.		Atc. Wt.	Sp. Grav.
Na	23	·97	K	39·1	·86
Cd	112	8·7	Tl	204	11·9
In	113·4	7·2	Pb	207	11·3

METALS.—6. IRON-COPPER GROUP.

SUB-GROUP A.

Aluminium, Al = 27·4.
Tetrad.   Salt type $(M_2)^{vi}Cl_6$.

Chromium, Cr = 52·5.
Hexad.   Salt types $M''Cl_2$ *and* $(M_2)^{vi}Cl_6$.

Manganese, Mn = 55 $\big\}$
Iron,   Fe = 56 $\big\}$
Hexad.   Salt types, $M''Cl_2$ *and* $(M_2)^{vi}Cl_6$

Cobalt, Co = 58·7 $\big\}$
Nickel, Ni = 58·7 $\big\}$
Tetrad.   Salt type, $M''Cl_2$.

These are white or grey metals of very high melting point. Their specific gravities follow one another in the same order as the atomic weights, and are almost directly proportional to them. Including copper, the solitary member of the next sub-group, they may be placed in the following order, which we shall show presently represents very fairly their mutual chemical relations :

Atomic Weights.		Specific Gravities.
27·4	Al	2·6
52·5	Cr	6·8 to 7·3

Atc. Wt.		Sp. Grav.	Atc. Wt.		Sp. Grav.
55	Mn	8·0 (about)	56	Fe	7·8
58·7	Co	8·9	58·7	Ni	8·6
			63·5	Cu	8·9

The metals of sub-group A resist atmospheric oxidation to a considerable extent, except moisture or carbonic acid be present. Several of them especially iron and manga-

nese, are capable of decomposing steam at a red heat with evolution of hydrogen. They all dissolve more or less rapidly in dilute acids.

Iron, cobalt, and nickel are strongly paramagnetic, chromium and manganese feebly so.

A synoptical view of the chemical relations of these metals to one another will best be obtained, since they are somewhat complex, by tabulating the formulæ of their most characteristic compounds.

Few observations upon the following table are necessary. As in all similar groups of intimately related elements, each one seems to affect a particular state of oxidation or com- bination in which it attains a condition of chemical repose or equilibrium. Thus the aluminic salts are absolutely irreducible to any lower state of oxidation ; chromic salts reducible with great difficulty ; ferric salts are easily transformed into ferrous, whilst manganic salts evolve chlorine or oxygen by mere ebullition. The isomor- phous relations of these metals to one another are of great interest, and are exhibited not only by the alums and other artificial salts, but in the constant association of these metals in nature, as, for example, in the replacement of aluminium by iron in clays, and in the silicates from which they are formed, in the replacement of the elements of ferric oxide by chromic oxide in chrome-iron, $FeO.Cr_2O_3$, and by the occurrence of metallic nickel in meteoric iron.

Several members of the group exhibit peculiarities which are well worthy of study, but in this place can receive only passing notice. Such, for example, are the metameric (?) modifications of alumina and of chromium salts, indicated in the latter case by curious changes of colour and solu- bility ; also the remarkable influence of a small quantity of carbon in increasing the fusibility and hardness of iron, nickel, cobalt, and, perhaps, others of the group ; also the production of an extensive series of ammoniacal bases by cobalt, not by nickel.

Al	Cr	Fe
No Aluminous Compounds known.	$CrCl_2$ $CrSO_47H_2O$? pale blue $\left.\begin{array}{l}CrSO_4\\K_2SO_4\end{array}\right\}\cdot 6H_2O$	FeO $FeCl_2$ $FeSO_4.7H_2O$ pale green $\left.\begin{array}{l}FeSO_4\\K_2SO_4\end{array}\right\}.6H_2O$
		isomorphous with
All Aluminic Compounds Colourless.		
Al_2O_3	Cr_3O_4	Fe_3O_4
	Cr_2O_3	Fe_2O_3
Al_2Cl_6 volatile.	Cr_2Cl_6 violet. volatile at red heat.	Fe_2Cl_6 green: volatile at red heat
$Al_2(SO_4)_3$	$Cr_2(SO_4)_3$	$Fe_2(SO_4)_3$
$AlK(SO_4)_2.12H_2O$	$CrK(SO_4)_2\cdot 12H_2O$	$FeK(SO_4)_2.12H_2O$
		modified
		$-(FeS_2)$
	CrO_2Cl_2	$-$
	CrO_3	$-$
	CrO_4K_2	FeO_4K_2
	CrO_4Ba	FeO_4Ba
	$\left\{\begin{array}{l}CrO_4K_2\\CrO_3\end{array}\right.$ or $\left\{\begin{array}{l}CrO_2.OK\\O\\CrO_2.OK\end{array}\right.$	$-$
	$\left\{\begin{array}{l}CrO_4K_2\\2CrO_3\end{array}\right.$ or $\left\{\begin{array}{l}CrO_2OK\\O\\CrO_2\\O\\CrO_2OK\end{array}\right.$	$-$
	$Cr_2O_6(OH)_2$?	$-$

Ni	Mn	Co

NiO
$NiCl_2$
$NiSO_4.7H_2O$
  bright green
	MnO
	$MnCl_2$
	$MnSO_4.7H_2O$
	  pale pink
		CoO
		$CoCl_2$
		$CoSO_4.7H_2O$
		  bright red

$\left.\begin{array}{l}NiSO_4\\K_2SO_4\end{array}\right\}$ ·6H$_2$O	$\left.\begin{array}{l}MnSO_4\\K_2SO_4\end{array}\right\}$ 6H$_2$O	$\left.\begin{array}{l}CoSO_4\\K_2SO_4\end{array}\right\}$ 6H$_2$O

corresponding magnesium salts.

—	Mn_3O_4	Co_3O_4
Ni_2O_2	Mn_2O_3	Co_2O_3
No Salts	Mn_2Cl_6 decomposed by heat	Co_2Cl_6 decomposed by heat
—	$Mn_2(SO_4)_3$?	$Co_2(SO_4)_3$?
—	$MnK(SO_4)_2 12H_2O$	—

cubes or regular octahedrons.

— (NiS_2)	MnO_2	—
—	MnO_2Cl_2	—
—	—	—
—	MnO_4K_2	—
—	MnO_4Ba	—
—	—	—
—	—	—
—	—	—
—	—	—
—	$Mn_2O_6(OH)_2$ $Mn_2O_6(OK)_2$	—

Atomicity of the Iron Group.

Manganese forms a sexfluoride, MnF_6, and a class of salts, the manganates, which are said to be isomorphous with the chromates and sulphates.   Hence manganese is sexivalent, and the formulæ of manganic perfluoride and potassic manganate may be written as follows :

$$
\begin{array}{ccc}
F & & F \\
\diagdown & & \diagup \\
F{-}Mn{-}F \\
\diagup & & \diagdown \\
F & & F
\end{array}
\qquad\qquad
\begin{array}{ccc}
KO & & O \\
\diagdown & & \diagup\!\diagup \\
& Mn & \\
\diagup & & \diagdown \\
KO & & O
\end{array}
$$
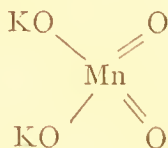
Manganese also forms a dioxide in which it is quadri-valent,

$$O = Mn = O,$$
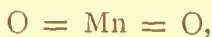
and a chloride corresponding with ferrous chloride in which it may be considered to be quadrivalent,

$$Cl_2Mn = MnCl_2.$$

or bivalent, $Cl - Mn - Cl$.   There is no direct evidence for either the one formula or the other, and, consequently, the latter is very commonly accepted for the sake of simplicity.

The permanganates must be represented by the formula $M'_2Mn_2O_8$, on the assumption of the hexad character of manganese, so that potassic permanganate becomes—

$$
\begin{array}{c}
O \\
\parallel \\
O = Mn{-}O{-}OK \\
\mid \\
O = Mn{-}O{-}OK \\
\parallel \\
O
\end{array}
$$

or,

$$
\begin{array}{c}
O \\
\parallel \\
O = Mn - OK \\
| \\
O \\
| \\
O \\
| \\
O = Mn - OK \\
\parallel \\
O
\end{array}
$$
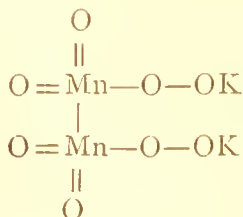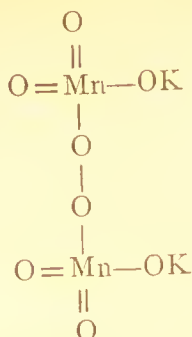
The alleged isomorphism of the permanganates and perchlorates remains unexplained.

By reason of the correspondence between the ferrates and manganates, iron must also be regarded as hexad; although in ferric, and probably also ferrous compounds, it is ordinarily tetrad.

Thus the vapour density of ferric chloride agrees with the half of the molecular weight denoted by the formula Fe_2Cl_6, although the formula $FeCl_3$ would equally well record its composition. The existence of iron pyrites, FeS_2, the analogue of SnS_2, also supports the hypothesis of the quadrivalence of iron in these compounds.

$$
\begin{array}{c}
Cl \quad Cl \\
| \qquad | \\
Cl - Fe - Fe - Cl \\
| \qquad | \\
Cl \quad Cl
\end{array}
\qquad\qquad
S = Fe = S
$$
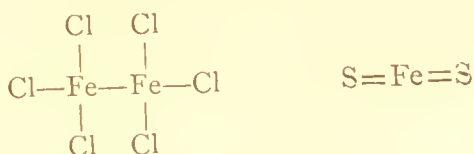
Chromium is also tetrad in its ordinary chromic salts, but hexad in the chromates, as well as in chromium sexfluoride, trioxide, and oxychloride.

$$
\begin{array}{c}
Cl \quad Cl \\
| \qquad | \\
Cl - Cr - Cr - Cl \\
| \qquad | \\
Cl \quad Cl
\end{array}
\qquad\qquad
\begin{array}{c}
KO \diagdown \qquad \diagup O \\
Cr \\
KO \diagup \qquad \diagdown O
\end{array}
$$
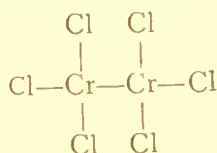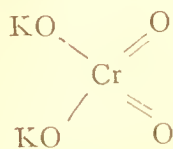
Chromic chloride.   Potassium chromate.

Aluminium manifests no tendency to form more than one chloride or oxide. It has been supposed triad, with the formula $AlCl_3$ for the chloride, but the isomorphism of alumina with ferric oxide and the vapour density of aluminic chloride point conclusively to the formulæ Al_2O_3 and Al_2Cl_6 for these two compounds.

$$O = Al - Al = O$$
$$\overset{O}{\diagup \diagdown}$$

Aluminic oxide.

$$Cl - Al - Al - Cl$$
with Cl Cl above and Cl Cl below

Aluminic chloride.
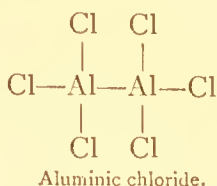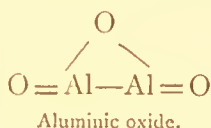
Cobalt and nickel are bivalent in their ordinary salts, but they form unstable peroxides, Co_2O_3 and Ni_2O_3, which lose oxygen at a red heat. These compounds, and the salts of the oxycobaltamines are almost the only known tetradic combinations of these two metals.

Sub-group B.

Copper, Cu = 63·5.
Diad. Salt-types, $(M_2)'' Cl_2$ *and* $M'' Cl_2$.

This metal is distinguished from the members of the series just considered by its red colour, by its very superior conductivity of heat and electricity, by its diamagnetic properties, by its ready oxidation when heated in dry air, and by the easy reduction of the metal from its oxide and salts, also by its indifference to diluted sulphuric or hydrochloric acid. It is further characterised by the formation of no oxide superior to the oxide CuO, by the production of a suboxide, Cu_2O, and corresponding series of salts, also by the facility with which all its compounds unite with or act upon ammonia. By the last two characters it indicates its relationship to silver and mercury.

The following are the most important of the compounds

of copper, together with the formulæ of compounds with which they manifest greater or less analogy :—

Cuprous.	Mercurous.	Argentic.
Cu_2O	Hg_2O	Ag_2O
or	or	

$$Cu'' \!\!\!\diagdown \!\!\! O \qquad Hg'' \!\!\!\diagdown \!\!\! O \qquad Ag' \!\!\!\diagdown \!\!\! O$$
$$Cu'' \!\!\!\diagup \qquad\quad Hg'' \!\!\!\diagup \qquad\quad Ag' \!\!\!\diagup$$

$$\begin{array}{ccc} Cu\!-\!Cl & Hg\!-\!Cl & \\ | & | & Ag\!-\!Cl \\ Cu\!-\!Cl & Hg\!-\!Cl & \end{array}$$

$$\begin{array}{ccc} Cu\!-\!H & & \\ | & \text{No hydride.} & \text{No hydride.} \\ Cu\!-\!H & & \end{array}$$

Cu_2S isomorphous with Ag_2S and with $CuAgS$.

Very few cuprous oxysalts are known, for when cuprous oxide is acted upon by acids it generally splits up and yields a cupric salt and a residue of metallic copper.

Cupric.	Iron and Manganese.
CuO	FeO
$CuSO_4.5H_2O$ isomorphous with $FeSO_4.5H_2O$	
	and with $MnSO_4.5H_2O$
$\left.\begin{array}{l}CuSO_4\\K_2SO_4\end{array}\right\}6H_2O$ isomorphous with $\left.\begin{array}{l}FeSO_4\\K_2SO_4\end{array}\right\}.6H_2O$	
CuS	FeS
$FeCuS_2$	
or $Fe_2Cu_2S_4$	FeS_2
Copper pyrites.	Iron pyrites.

Considering the very general blue or green colour of the cupric salts, and their dissolution in excess of ammonia to form a blue liquid, copper approaches more nearly to nickel than to any other member of the iron group. And although a pentahydrated nickel sulphate corresponding with common blue vitriol has not been described, yet of the isomorphism of copper and nickel in the form of sulphate there can be no

doubt. For when a mixture of cupric and nickel sulphates is crystallised, the crystals which are deposited, though containing both nickel and copper, have the form of nickel sulphate, and contain seven molecules of water when the nickel is in excess. If, on the other hand, the cupric sulphate is in excess, the crystals have the form of blue vitriol and contain five molecules of water.

Through the isomorphism of the double potassio-sulphates, the iron-copper group of metals is connected with the zinc group previously described.

METALS.—7. PLATINUM GROUP.

SUB-GROUP A.—GOLD.

Triad. Salt types $(M_2)^{''}Cl_2$ *and* $M^{'''}Cl_3$.

Gold is a metal of familiar yellow colour and high specific gravity. In consideration of its inalterability in the fire or by the action of acids (save nitro-muriatic acid, hence called *aqua regia*), gold was regarded by the old chemists as the type of a " noble " metal. It forms two classes of salts, of which the aurous are somewhat unstable, readily undergoing decomposition into an auric compound and metallic gold. The sodio-aurous theiosulphate $\left.\begin{array}{c}Na_6\\Au_2\end{array}\right\}(S_2O_3)_4.4H_2O$ is one of the most definite.

The trichloride is the most important auric compound. It is a red, crystalline, deliquescent body, which forms yellow crystallisable compounds with the chlorides of hydrogen and the alkali-metals, $HAuCl_4$, $KAuCl_4$, NH_4AuCl_4, etc.

Gold is reduced from its solutions with the greatest readiness by nitrous acid, sulphurous acid, ferrous salts, and all reducing agents, including many organic substances. Its oxides and chlorides also yield up the metal when strongly heated.

Sub-group B.

The members of this group range themselves very natu-rally into two divisions, each of which exhibits a striking uniformity of atomic weight and specific gravity. With one of these gold allies itself, in virtue of its high specific gravity and atomic weight, as well as its resistance to oxidation and solution in acids ; also by the yellow colour of its com-pounds and the tendency of its highest chloride to form double salts. With the other, silver is, perhaps, in a similar manner, remotely connected, though in this case it must be admitted there is but little in the properties of the metal to sanction such an arrangement.

	Symb.	At. Wt.	S.G.		Symb.	At. Wt.	S.G.
Silver	Ag	- 108	10·5	Gold	Au	- 197	19·3
Monad				*Triad*			
Palladium	Pd	- 106·5	11·8	Platinum	Pt.	- 197·5	21·5
Rhodium	Ro	- 104·5	11·0	Iridium	Ir	- 197	21·1
Ruthenium	Ru	- 104·5	11·4	Osmium	Os	- 199	21·4
Tetrad				*Tetrad*			

The true platinum metals are white metals which require for their fusion the highest attainable temperatures of the oxyhydrogen flame. It is stated, indeed, that osmium has never been really melted ; hence the numbers by which their respective specific gravities are denoted can only be approxi-mately correct.

They differ somewhat in their behaviour towards re-agents. Palladium, for example, is slowly dissolved by nitric acid, whilst some of the others resist the action even of *aqua regia*. Ruthenium and osmium, on the other hand, although slowly attacked by *aqua regia* when in the compact state, undergo oxidation somewhat rapidly when heated in the air.

They all, with the exception of rhodium, form more or less stable tetrachlorides, which are generally yellow and easily reducible by heat, either to the metallic state or to

lower chlorides. These compounds also unite with the chlorides of the alkali-metals, forming crystallisable salts, which in some cases as, for example, the platinochlorides of potassium and ammonium,

$$2KCl.PtCl_4 \text{ or } K_2PtCl_6$$
$$2NH_4Cl.PtCl_4 \text{ or } (NH_4)_2 PtCl_6$$
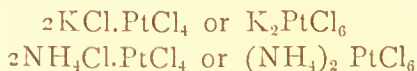
are almost insoluble and highly characteristic. But besides these tetrachlorides, the platinum metals yield dichlorides and sesquichlorides, which are in special cases of greater importance. The dichloride of palladium, for example, is one of its most important compounds, and far more stable than the tetrachloride, which is known only in a state of solution, and in its double salts. Rhodium again forms only one chloride, and that the sesquichloride.

The following are all the definite chlorides of these metals which have been described :—

Dichlorides.	Sesquichlorides.	Tetrachlorides.
$PdCl_2$	—	$PdCl_4$
$PtCl_2$	—	$PtCl_4$
—	Ro_2Cl_6	—
$IrCl_2$?	Ir_2Cl_6	$IrCl_4$
$RuCl_2$	Ru_2Cl_6	$RuCl_4$
$OsCl_2$	Os_2Cl_6	$OsCl_4$

Ruthenium and osmium are specialised by the existence of potassium salts called rutheniate and osmiate, which contain the elements of potassium oxide, together with a trioxide of ruthenium or osmium.

$$K_2O.RuO_3 \text{ or } K_2RuO_4.$$
$$K_2O.OsO_3 \text{ or } K_2OsO_4.$$
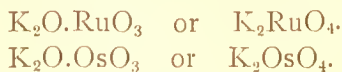
The trioxides, or anhydrides, are not known in an isolated state. But the most remarkable compounds of these metals are the tetroxides RuO_4, OsO_4, which are highly volatile bodies, soluble in water to form acid solu-

tions, but apparently incapable of generating salts. The constitution of these compounds is not well understood. They are the only tetroxides known.

EXERCISES ON SECTION IV.

1. What experiments and reasoning would lead you to regard chlorine as a monad element?

2. In what respects does iodine resemble and differ from bromine?

3. Discuss the title of hydrogen to be considered (*a*) a non-metal; (*b*) a metalloid.

4. Classify the solid elements according to their specific gravities.

5. What are the properties which distinguish chlorine, and the elements most like chlorine, from potassium, and the elements which are most like potassium?

6. Compare and contrast the elements phosphorus and arsenic, both in their physical and chemical properties.

7. What are the special characteristics of carbon which distinguish it from other elements?

8. Describe as many as you can of the modified forms of carbon, sulphur, and phosphorus.

9. What acids are known consisting of hydrogen, oxygen, and phosphorus? Give their graphic constitutional formulæ, and point out the basicity of each.

10. What differences and analogies exist between the corresponding compounds of potassium and sodium?

11. To what elements does mercury present the greatest resemblance? Point out instances of analogy in properties.

12. Show by a comparison of their compounds in what respects the elements carbon, silicon, tin, and lead may be said to constitute a natural group.

13. Give the formulæ, simple and constitutional, of the following compounds:—common salt, caustic potash, sulphuric acid, baryta, barium peroxide, lead peroxide, iron peroxide, silver phosphate, silver arsenate, silver arsenite, kakodyl, and tartar-emetic.

14. Give a full account of the two oxides of nitrogen known as nitric oxide and nitric peroxide respectively.

15. Give instances of compounds which do not comply with the law of even numbers.

16. What are the chief points of resemblance and difference between the corresponding calcium and magnesium compounds?

17. Assign a place among the elements to each of the following bodies :—copper, nitrogen, boron, thallium, vanadium, gold.   Give full reasons in each case.

18. The constitution of phosphorus compounds has been explained on the assumption of the trivalence of the phosphorus atom.   Discuss this view.

19. By what arguments would you support the number 32 against the number 16 as the atomic weight of sulphur?

20. Caustic potash is often said to be formed upon the water type. Explain this.

21. What is an alum?   At the temperature of 180δ common alum loses $\frac{2}{7}$ of its water.   How may this fact be brought to bear upon the construction of its formula?

22. Classify some of the better known elements according to their atomicity, mentioning and explaining as far as possible doubtful cases.

23. Write the formulæ of orthosulphuric acid and some of its salts. An ortho-acid may be defined as one in which the characteristic element (sulphur in this case) is saturated with hydroxyl.

24. One gram of phosphorus yields 2·903 grams of phosphoric anhydride.   Will this enable you to determine the atomic weight of the element?   and, if not, what further data are necessary?

25. How much phosphorus is contained in 120 lb. of bone-ash, consisting of $Ca_3 (PO_4)_2$, 88·5 parts, and $Ca\ CO_3$, 11·5 parts, in 100?

26. What weight of phosphorus is contained in 10 litres of phosphorus vapour at 1040°?   Pressure normal.

27. What weight of phosphorus is contained in 10 litres of phosphine at 12°?   Pressure normal.

28. No volatile compound appears to be known of which two volumes of vapour contain less than 55 parts by weight of aluminium. Why is not the usual atomic weight of aluminium doubled?

29. Calculate the percentage composition of cryolite, Na_3AlF_6.

30. How many kilograms of litharge can be obtained from 40·5 kilos of lead, and what volume of oxygen measured at 20° and under 765 mm. is absorbed in the process?

SECTION V.

CHAPTER XXIV.

CLASSIFICATION OF COMPOUNDS.

ACIDS, BASES, SALTS.

Acids.—The only element common to all acids is hydro-
gen, and the characteristic property of this hydrogen is its
ready exchangeability for a metal. It does not appear that
this is due to any peculiarity of the hydrogen itself, but ·
to the fact that, in all well-defined acids, it is associated
with other elements of very eager affinities. Acids may be
divided into two classes according as oxygen does or does not
enter into their composition. The latter class is necessarily
very small, and the following list includes nearly all the unoxi-
dised acids known :—

Hydrofluoric acid	HF.
Hydrochloric acid	HCl.
Hydrobromic acid	HBr.
Hydriodic acid	HI.
Hydrocyanic acid	HCN
Hydrosulphuric acid	H_2S.

It is important to remark, however, that although such a
distinction may for certain purposes be occasionally recog-
nised, there is no essential difference between acids which
contain oxygen and those which do not.

Now, it is obvious that the activity with which hydro-
chloric acid, for example, produces salts when in contact
with suitable metals, is due to the elective attraction of the

chlorine for the metal, and that hydrocyanic acid, a molecule of which contains the same quantity of hydrogen, does not act upon metals with the same promptitude, because the cyanogen group has not the same attraction for metals as chlorine.

The chemical energy of an acid, then, does not depend upon the hydrogen which it contains, but upon the electronegative character more or less strongly marked in the elements with which the hydrogen is associated. It is a very remarkable fact, however, that the existence of hydrogen in a body, in the position which it occupies in acids, namely, in the position of a base, does confer upon the compound one very general characteristic, and that is a sour taste. The sourness of soluble hydrogen salts would, perhaps, have been considered no more remarkable than the astringency of iron salts, the bitterness of magnesium, or the sweetness of glucinum compounds, but that it constitutes a character which serves to differentiate real acids from bodies such as ammonia, alcohols, and metallic hydrates, which all resemble acids so far as to exchange, under certain circumstances, part of their hydrogen for metals.

Oxyacids are bodies of very varied character. Some considerations concerning them have already been dwelt upon in the article on oxygen (Chap. XXI., p. 183).

With regard to the properties of acids in general, sufficient has already been written in the article on hydrogen (Chap. XXII., p. 199). It now only remains, therefore, to discuss that property of acids known as " basicity." This inquiry amounts in some cases to a determination of the weight of the molecule, and reference has already been made to an example of the kind in the article on molecular weights (Chap. XVI., p. 127). The question is, however, one of great importance, and deserves to be examined a little more in detail. The basicity of an acid depends upon the number of atoms of hydrogen directly exchangeable out of each molecule for metallic atoms · an acid containing one such atom

of hydrogen being called monobasic, one containing two such atoms is dibasic, or three, tribasic, and so on. We may infer the basicity of a given acid from the number of distinct salts it is capable of yielding with each metal. Monobasic acids generally give one salt, dibasic acids, as shown in the case of sulphuric acid, give two, and tribasic acids give three. Mere inspection of the formula of an acid does not, however, furnish sufficient information upon which to form a judgment regarding the basicity of the acid and the number of salts it is capable of producing ; for it by no means follows, from the existence of two or three atoms of hydrogen in the molecule, that it should be dibasic or tribasic. The basicity depends not upon the total number of hydrogen atoms present, but upon the total number endowed with this particular power of metallic exchange.

The three following acids of phosphorus afford an example of this. Each molecule contains three atoms of hydrogen, but the first is monobasic, the second dibasic, the third tribasic :—

Hypophosphorous acid .	H_3PO_2 or HPH_2O_2
Phosphorous acid	. H_3PO_3 or H_2PHO_3
Phosphoric acid	. H_3PO_4

In this and similar cases it has been generally observed that increase of basicity, as well as of sourness and general chemical acidity, accompanies the addition of oxygen. Hence it has been inferred that those atoms of hydrogen which are exchangeable for metals are combined more intimately with oxygen than others which are not similarly exchangeable. On this hypothesis the formulæ of the three acids referred to above are represented in the following manner :—

$$\text{Hypophosphorous acid} \quad O=\overset{\displaystyle H \quad H}{\underset{}{P}}-OH$$

Phosphorous acid

$$O = P \underset{\diagdown OH}{\overset{\diagup OH}{\overset{| \ H}{}}}$$

Phosphoric acid .

$$O = P \underset{\diagdown OH}{\overset{\diagup OH}{-OH}}$$
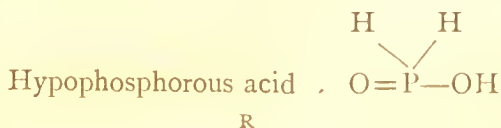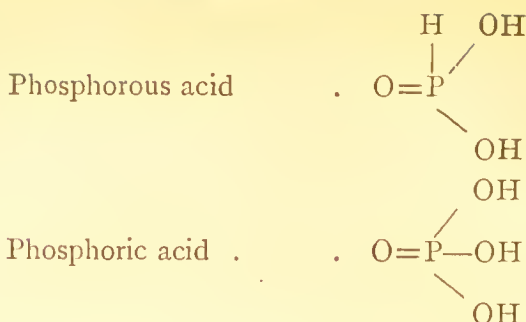
But acids are capable of undergoing a variety of modifi-
cations under the influence of re-agents, and some of these
are available as evidence towards the establishment of their
basicity. It has been found, for example, that acids which
possess only one basic atom of hydrogen, or are monobasic,
yield only one amide and one chloride. Acetic acid, for
example, gives the following derivatives, the relation of
which to acetic acid is obvious from the formulæ :—

<div align="center">

Acetic acid   .   . $HO.C_2H_3O$

Acetyl chloride .   . $Cl.C_2H_3O$

Acetamide   .   . $NH_2.C_2H_3O.$

</div>

Dibasic acids give two derivatives of the same kind, and
tribasic acids give three.

We may now resume the case of sulphuric acid adverted
to in Chap. XVI. as a very instructive example.

The simplest formula for sulphuric acid is H_2SO_4. The
problem before us is to prove that this formula, with the
relative weight 98, is the formula of the molecule, and that
the acid is dibasic.

1. The fact of the existence of two classes of sulphates
has been already appealed to. It is clear that the whole
of the hydrogen of the acid is replaceable by metals, and
that it is capable of replacement one half at a time. We
arrive then at such formulæ as these :

$$\left. \begin{matrix} Na \\ H \end{matrix} \right\} SO_4 \qquad \left. \begin{matrix} Na \\ Na \end{matrix} \right\} SO_4 \qquad \left. \begin{matrix} K \\ K \end{matrix} \right\} SO_4 \qquad \left. \begin{matrix} K \\ Li \end{matrix} \right\} SO_4$$
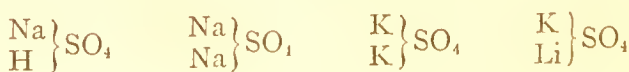
Evidence of this kind is almost conclusive, but it happens that in the present instance other testimony is abundant.

2. Thus we might show that sulphuric acid is produced when sulphur trioxide and water, both bodies of known molecular weight, unite together.

$$SO_3 \quad + \quad OH_2 \quad = \quad SO_4H_2.$$

3. Also, when sulphur dioxide is dissolved in water and the solution exposed to the air—

$$SO_2 \quad + \quad OH_2 \quad + \quad O \quad = \quad SO_4H_2.$$

4. It is also formed by the direct union of hydrogen peroxide and sulphur dioxide—

$$SO_2 \quad + \quad O_2H_2 \quad = \quad SO_4H_2.$$

A sulphate being generated in the following strictly parallel case of combination—

$$PbO_2 \quad + \quad SO_2 \quad = \quad SO_4Pb.$$

5. Sulphuric acid is generated by the decomposition of sulphuryl chloride by water—

$$SO_2Cl_2 \quad + \quad 2H_2O \quad = \quad SO_4H_2 \quad + \quad 2HCl.$$

According to equations 2, 3, 4, the whole of the acting materials enter into the composition of the sulphuric acid which is produced, and therefore there is a strong probability in favour of the molecular weight of sulphuric acid being the sum of their separate molecular weights. Similar considerations apply to equation 5. The molecule of sulphuric acid is here shown to be built up of the molecules of the sulphur oxychloride and water, minus two atoms of hydrogen and two atoms of chlorine.

6. We now come to some reactions in which various constituents of the sulphuric acid molecule are replaced. When the acid is heated with phosphoric chloride, two successive reactions of the same kind ensue. In the first

an atom of chlorine is introduced in place of the group (OH) which is removed.

$$H_2SO_4 + PCl_5 = HClSO_3 + POCl_3 + HCl.$$

And this kind of exchange is repeated in the second reaction :

$$HClSO_3 + PCl_5 = Cl_2SO_2 + POCl_3 + HCl.$$

The relation of the two new chlorides to sulphuric acid may be exhibited most satisfactorily by writing the formulæ in the following manner :—

$$\begin{matrix} HO \\ HO \end{matrix} SO_2 \qquad \begin{matrix} HO \\ Cl \end{matrix} SO_2 \qquad \begin{matrix} Cl \\ Cl \end{matrix} SO_2$$

Sulphuric acid or   Sulphuryl chlor-   Sulphuryl
Hydrate.   hydrate.   chloride.
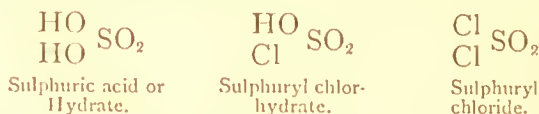
7. Two " amides," standing in the same kind of relationship towards sulphuric acid, also exist. Their formulæ may be written thus :—

$$\begin{matrix} HO \\ HO \end{matrix} SO_2 \qquad \begin{matrix} HO \\ NH_2 \end{matrix} SO_2 \qquad \begin{matrix} NH_2 \\ NH_2 \end{matrix} SO_2$$

Sulphuric acid.   Sulphamic acid.   Sulphamide.

The existence of these compounds and the corresponding chlorides supplies evidence similar to that deducible from a knowledge of the acid and double sulphates (1). These facts tend to show that the hydrogen contained in a molecule of sulphuric acid is divisible into two equal parts, and that these two hydrogen atoms are probably more closely united with two atoms of oxygen than with other constituents of the molecule.

8. When concentrated sulphuric acid is made to act on certain hydrocarbons, alcohols, phenols, and other bodies, compounds are produced which have the properties of monobasic acids. These compounds are in some degree analogous to salts ; at any rate, sulphuric acid could not produce derivatives of this kind if it did not contain at least two atoms of basylous hydrogen.

$$C_6H_6 + H_2SO_4 = H_2O + C_6H_5(SO_3H)$$

Benzene.   Sulphuric acid.   Water.   Benzene-sulphonic acid.

$$C_2H_5OH + H_2SO_4 = H_2O + C_2H_5O(SO_3H)$$

Ethylic alcohol.   Sulphuric acid.   Water.   Ethyl-sulphuric acid.

$$C_6H_5OH + H_2SO_4 = H_2O + C_6H_4(OH)(SO_3H)$$

Phenol.   Sulphuric acid.   Water.   Phenol-sulphonic acid.
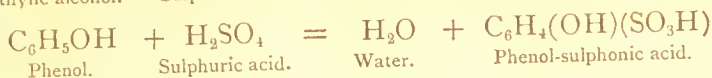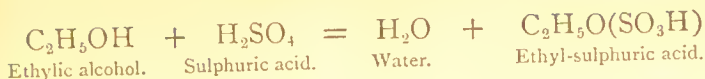
All the foregoing facts point to the same conclusion, and it matters not whether we write the formula of sulphuric acid :—

$$H_2SO_4 \text{ or } \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 \text{ or } (HO)_2SO_2 \text{ or } H_2O.SO_3,$$
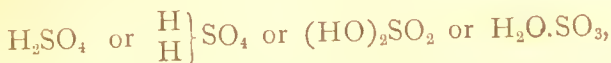
in the attempt to record one or other of its various modes of formation or decomposition. These different expressions represent one and the same molecular weight.

In one respect, which has not yet been referred to, there is a difference between acids which contain oxygen and those which do not contain that element. Compounds in which there is no oxygen cannot by any possibility be made to yield water. Hence there are no anhydrides corresponding to the haloid acids. Oxyacids, however, may, in various ways, be made to furnish water and an oxide, which is called an *anhydride*. Thus sulphurous acid splits up readily in the following manner :—

$$H_2SO_3 = H_2O + SO_2$$

Sulphurous acid.   Water.   Sulphurous anhydride.
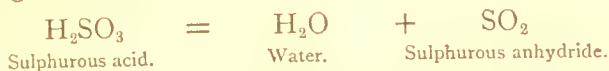
Dibasic acids give their anhydrides most readily when simply heated, whereas monobasic acids generally require to be treated with some dehydrating agent. This may, perhaps, be connected in some way with the fact that a dibasic acid always contains within itself the elements of water, whilst a monobasic acid cannot generate water except by the combined action of two molecules.

Dibasic.

$$H_2CO_3 = H_2O + CO_2$$

Carbonic acid.   Anhydride.

$$H_2C_4H_4O_4 = H_2O + C_4H_4O_3$$

Succinic acid.   Anhydride.

Monobasic.

$$\left.\begin{array}{l}HNO_3 \\ HNO_3\end{array}\right\} \quad = \quad H_2O \quad + \quad N_2O_5.$$
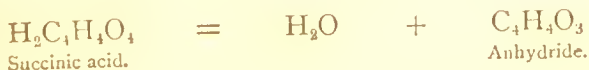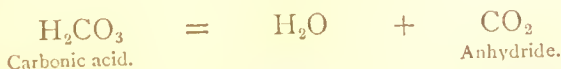
Nitric acid.   Anhydride.
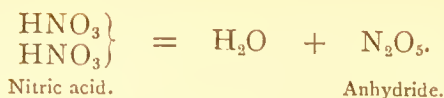
In the case of some monobasic acids, the anhydride can only be obtained by a succession of operations. In order to prepare acetic anhydride, for example, the chloride is first made from the acid, and this compound is then allowed to react upon a salt.

$$C_2H_3OCl \quad + \quad C_2H_3O.ONa \quad = \quad NaCl \quad + \quad (C_2H_3O)_2O$$

Acetic chloride.   Sodium acetate.   Sodium   Acetic oxide or
                                         chloride.   anhydride.
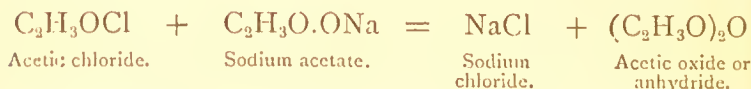
This difference between monobasic and dibasic acids is, however, not sufficiently general to be maintained as a distinction of any practical importance.

Bases.—The idea implied by the word " base " belongs to the obsolete dualistic theory of salts. According to this theory, every salt was supposed to be made up of two parts, one of which, consisting of a metallic oxide, formed the base ; whilst the other part, usually the oxide of a non-metal, or some group consisting of carbon, hydrogen, and oxygen, was regarded as the acid. Sulphate of soda, for example, was, according to dualistic phraseology, composed of the base soda or oxide of sodium, and sulphuric acid or trioxide of sulphur, and its formula was written $NaOSO_3$, or, adopting modern atomic weights, Na_2OSO_3.

Now, although this idea has been considerably modified, and we no longer look upon a salt as a double structure of this kind, the fact remains that those oxides of metals which are not overcharged with oxygen do agree in the property of uniting or reacting with acids, so as more or less com-pletely to neutralise them. And this property is shared by the hydrates corresponding with these oxides. Adopting the old name, and taking this neutralising faculty as the

criterion of the basic function of oxides, we may define a base as *a metallic oxide or hydrate capable of saturating acids.*

It will be noticed that a basic hydrate and basic oxide have the same relation to each other as an acid and its anhydride, and consequently it would be quite reasonable to speak of the anhydrous oxide as an anhydride, reserving the term base for the hydrate.   For example :—

$$2HNO_3 \quad - \quad OH_2 \quad = \quad N_2O_5$$
Acid.   Water.   Acid anhydride.

$$2KHO \quad - \quad OH_2 \quad = \quad K_2O$$
Basic hydrate or base.   Basic oxide or basic anhydride.

$$H_2SO_4 \quad - \quad OH_2 \quad = \quad SO_3$$
Acid.   Water.   Acid anhydride.

$$Ca(HO)_2 \quad - \quad OH_2 \quad = \quad CaO$$
Basic hydrate or base.   Water.   Basic oxide or basic anhydride.
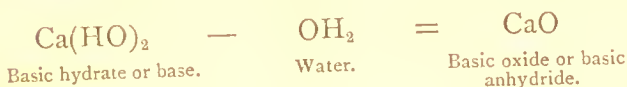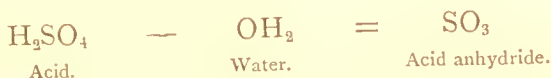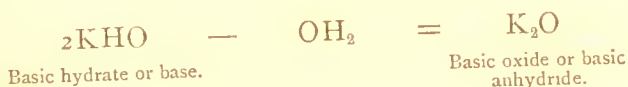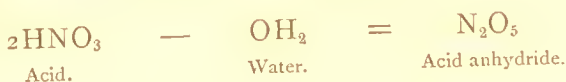
It must not be forgotten that ammonia and a certain class of its derivatives also possess the power, in a remarkable degree, of uniting with acids and forming perfectly neutral compounds, which present all the external characteristics, and many of the chemical properties, of ordinary salts.   Ammonia and the alkaloids are therefore commonly regarded as bases, though it is well to remind the student that these bodies differ from metallic oxides or hydrates in their reactions, both with acids and with anhydrides.   Thus with acids, ammonia enters into direct combination, without the formation of any secondary product, thus :—

$$NH_3 \quad + \quad HNO_3 \quad = \quad NH_3HNO_3$$
$$\text{or } NH_4NO_3$$
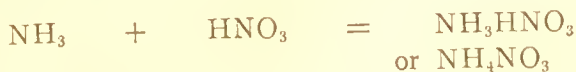
Whereas basic oxides or hydrates invariably generate water in addition to the salt.*

$$\underset{\text{Base.}}{KHO} + \underset{\text{Acid.}}{HNO_3} = \underset{\text{Salt.}}{KNO_3} + \underset{\text{Water.}}{H_2O}$$

Again, ammonia combines with acid anhydrides generally, but the compounds which result are not salts, whilst a basic oxide under the same circumstances always yields a salt of the ordinary type. For example :—

$$BaO + SO_3 = BaSO_4$$

Such a reaction is obviously the counterpart of that which occurs when an acid or hydrogen salt is formed from water and the anhydride.

$$H_2O + SO_3 = H_2SO_4$$
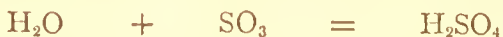
The general property of neutralising acids is associated, in the case of all those bases which are soluble in water, with a peculiar soapy taste, and with a power of affecting vegetable colours. The reds are changed to blue or green, the blues to green, and the yellows to brown or brownish red. In litmus the alteration of tint characteristic of alkaline reaction is the result of the conversion of the feeble litmus acid (red) into a blue salt. Somewhat similar changes probably occur in other cases.

Salts.—It has been stated that an acid is a body in which hydrogen is united with a strongly electro-negative element or group of elements. When such a body is acted upon by a metal or metallic oxide, the hydrogen is exchanged for a metal, or something equivalent to it, and a salt is formed. We may define a salt, then, as a compound in which a metallic or other radicle of like nature is combined with

---

* The demonstration of this fact is very generally neglected by teachers. An easy experiment by which an appreciable quantity of water may be collected in a few minutes consists in passing dry hydrochloric acid over gently-heated litharge.

a radicle of more or less decided electro-negative character. It has already been explained that electro-negative elements are those which in the electrolysis of the salt are collected at the positive electrode, and which by uniting with hydrogen form acids. In short, the radicles which, in union with hydrogen, form acids, and with metals form salts, are always composed either of the non-metallic, or, as they are called in this book, oxygenic elements, or of certain metals in company with a relatively large quantity of oxygen.

A considerable number of salts are known in which a part of the acid radicle of the normal compound is replaced by oxygen or hydroxyl. Such compounds are often called basic salts. The following are some examples which serve to show the general character of these compounds :—

Plumbic chloro hydrate	$Pb \begin{cases} OH \\ Cl \end{cases}$
Plumbic hydrate nitrate	$Pb \begin{cases} NO_3 \\ OH \end{cases}$
Bismuthic hydrate nitrate	$Bi \begin{cases} NO_3 \\ NO_3 \\ OH \end{cases}$
Ferric oxysulphate	$Fe_2 \begin{cases} (SO_4)_2 \\ O \end{cases}$
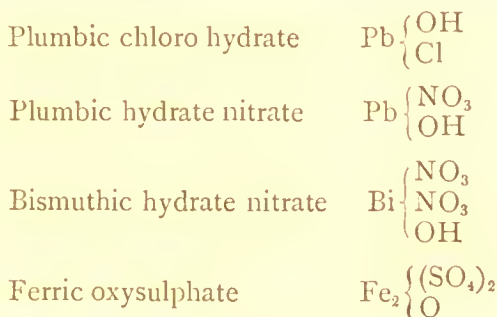
Salts may be formed in a variety of ways, amongst which are the following :—

(*a*) Union of elements,

$$Na_2 \quad + \quad Cl_2 \quad = \quad 2NaCl.$$
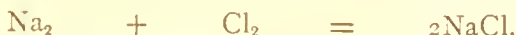
(*b*) Union of acid and basic oxide,

$$CaO \quad + \quad CO_2 \quad = \quad CaCO_3.$$
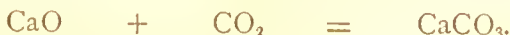
(*c*) Action of metal on acid,

$$Zn \quad + \quad H_2SO_4 \quad = \quad ZnSO_4 \quad + \quad H^2$$

(*d*) Action of metallic oxide or hydrate on acid,

$$ZnO + H_2SO_4 = ZnSO_4 + OH_2$$
$$NaHO + HNO_3 = NaNO_3 + OH_2$$

(*e*) Double decomposition between two salts.

$$BaCl_2 + Na_2HPO_4 = 2NaCl + BaHPO_4$$

As regards the properties of salts no very general state-
ments can be made. Liquid and solid, soluble and in-
soluble, crystalline and uncrystallisable bodies are alike in-
cluded under this denomination, so that no comparison can
now be instituted between the bodies thus named by the
chemist and that substance which was probably the proto-
type of all salts, namely, *common salt* (Gr. ἅλς, Lat. *sal*, Fr.
sel, Ger. *salz*).

In the production of salts the potential energy of the re-
acting materials is more or less exhausted, so that salts are
generally bodies of feeble attractions. We observe this in
the comparatively small number of compounds into which
entire salts enter, and the facility with which such combina-
tions are broken up.

CHAPTER XXV.

DERIVATIVES OF AMMONIA.

Ammonium Theory.—Ammonia is excessively soluble in
water, and the solution has all the properties of a powerful
alkali. Like caustic potash, it restores the blue colour to
litmus, which has been reddened by an acid, it absorbs car-
bonic acid from the air, it saturates acids forming a class of
crystallisable neutral salts, which are isomorphous with the
corresponding salts of potassium. Like potash also it pre-
cipitates hydrates when added to the solutions of a great
many metallic salts, though in a few cases, *e.g.*, with mer-

curic salts, it gives rise to compounds of a different character. Lastly, solution of ammonia differs from solution of caustic potash in that when evaporated it leaves no residue. In consequence of this want of stability, solution of ammonia is often referred to as the *volatile alkali*.

Guided by this marked resemblance between the compounds of ammonia and those of potassium, chemists have been led to regard both series as constituted in the same manner. Writing down in parallel columns a list of ammoniacal and potash salts, and eliminating from each pair of formulæ the symbols which are common to them both, we find that the group composed of one atom of nitrogen and four atoms of hydrogen, NH_4, is the residue left over in the one case, whilst the solitary symbol K remains in the other. The latter represents the radicle potassium, which, when isolated, presents all the characteristics of a metal. The conclusion seems almost inevitable that the radicle NH_4 would also exhibit metallic lustre, conductivity, and so forth, if it could be obtained in a free state. In anticipation of this hypothesis being confirmed, it has been called *ammonium.*

Compounds of

Ammonium.			Potassium.
$NH_3.H_2O$	or NH_4HO	or $AmHO$	KHO
$NH_3.HCl$	or NH_4Cl	or $AmCl$	KCl
$NH_3.HNO_3$	or NH_4NO_3	or $AmNO_3$	KNO_3
$NH_3.H_2SO_4$	or NH_4HSO_4	or $AmHSO_4$	$KHSO_4$
$(NH_3)_2.H_2SO_4$	or $(NH_4)_2SO_4$	or Am_2SO_4	K_2SO_4
$NH_3H_3PO_4$	or $(NH_4)H_2PO_4$	or AmH_2PO_4	KH_2PO_4
$(NH_3)_2H_3PO_4$	cr $(NH_4)_2HPO_4$	or Am_2HPO_4	K_2HPO_4
$(NH_3)_3H_3PO_4$	or $(NH_4)_3PO_4$	or Am_3PO_4	K_3PO_4

A curious phenomenon occurs when a lump of sodium amalgam is placed in a solution of sal-ammoniac, or when the same salt, dissolved in water, is submitted to electrolysis, a globule of mercury being employed as the negative electrode. The mercury swells enormously, becoming so light as to float in the solution, without at the same time

losing altogether its metallic aspect. In a few minutes, how-
ever, the spongy mass again contracts, hydrogen and am-
monia make their escape, and the mercury recovers its
original volume and lustre. The body thus produced was
long regarded as a true compound of mercury with the
hypothetical metallic radicle, and as such received the name
ammonium amalgam. It has been shown, however, that
the mercury whilst in this condition yields to pressure in
the same way as froth, and that the phenomenon is really
due, not to the formation of an amalgam, but to the
mechanical distension of the mercury by gas.

The radicle ammonium has, in fact, never been isolated,*
and there is no great probability of its ever being obtained.
The ammonium theory finds a sufficient basis in the iso-
morphism of the ammonia and potash salts, and the general
resemblance of the hydrate and its derivatives (to be men-
tioned presently) to the fixed alkalis, and the theory itself
should be regarded merely as a summary and memorandum
of these relations.

Amines.—The hydrogen of ammonia admits of substitu-
tion in three successive stages, and the compounds thus
formed are believed to be constituted in the same manner
as ammonia itself, or, using the ordinary expression, they
belong to the ammonia type,

$$N \begin{cases} H \\ H \\ H \end{cases}$$

the replacing radicles being severally combined with the
nitrogen in the same manner as the hydrogen atoms of the
type.

When positive radicles, consisting of metals or hydro-
carbons, are substituted for the hydrogen in the ammonia
molecule, the resulting compounds retain the alkalinity and
general basic character of ammonia. Such compounds are

* Notwithstanding statements to the contrary.

called *amines*. They generally combine with acids, but are unaffected by treatment with alkalies. There are several classes of amines resulting from the more or less extensive replacement of the hydrogen or the coalescence of two or more molecules of ammonia. Their constitution will be understood after inspection of the following table, in which the symbol R represents a positive radicle, the valency of which is indicated by dashes : —

Monamines.	Diamines.	Triamines.
Primary. $N \begin{cases} R' \\ H \\ H \end{cases}$	Primary. $N_2 \begin{cases} R'' \\ H_2 \\ H_2 \end{cases}$	Primary. $N_3 \begin{cases} R''' \\ H_3 \\ H_3 \end{cases}$
Secondary. $N \begin{cases} R' \\ R' \\ H \end{cases}$	Secondary. $N_2 \begin{cases} R'' \\ R'' \\ H_2 \end{cases} \quad N_2 \begin{cases} R'' \\ R'_2 \\ H_2 \end{cases}$	Secondary. $N_3 \begin{cases} R''' \\ R''' \\ H_3 \end{cases} \quad N_3 \begin{cases} R''' \\ R'_3, \\ H_3 \end{cases}$ etc.
Tertiary. $N \begin{cases} R' \\ R' \\ R' \end{cases}$	Tertiary. $N_2 \begin{cases} R'' \\ R''N_2 \\ R'' \end{cases} \begin{cases} R'' \\ R''N_2 \\ R'_2 \end{cases} \begin{cases} R'' \\ R'_2 \\ R'_2 \end{cases}$	Tertiary. $N_3 \begin{cases} R''' \\ R'''N_3 \\ R''' \end{cases} \begin{cases} R''' \\ R'''N_3 \\ R'_3 \end{cases} \begin{cases} R'' \\ R'_3 \\ R'_3 \end{cases}$ etc.

Monamines are capable of saturating only one molecule of a monobasic acid, but diamines unite with two, and triamines with three molecules of such acids. The diamines and triamines also yield intermediate compounds. Representing the monamines, diamines, and triamines respectively by the symbols Am, Am^2 and Am^3, the general formulæ of the chlorides may be written in the following manner :

$$Am.HCl \qquad Am^2.HCl \qquad An^3.HCl.$$
$$Am^2.2HCl \qquad Am^3.2HCl.$$
$$Am^3.3HCl.$$
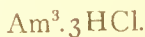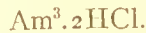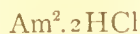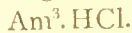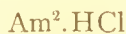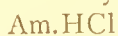
The tertiary amines unite with iodides and other salts of alcohol radicles in the same manner as with acids, fur-

nishing compounds which may be formulated either as
ammonia compounds or as derived from the hypothetical
ammonium radicle.   Thus triethyl-amine combines with
ethyl iodide, forming a crystalline compound, which may
be represented either as $N(C_2H_5)_3 . C_2H_5I$, or, more con-
sistently and conveniently, as tetrethyl-ammonium iodide
$N(C_2H_5)_4I$.   This compound is obviously the analogue of
ammonium iodide.   When acted upon by silver oxide and
water, it exchanges iodine for hydroxyl, and gives rise to a
hydrate of tetrethyl-ammonium, $N(C_2H_5)_4HO$, a compound
which may be obtained in the solid state, and which in its
causticity and alkalinity closely resembles potassic hydrate.
The existence of this compound, and others of similar
nature, furnishes strong evidence in favour of the ammonium
theory.   Like their hypothetical prototype, however, the
substituted ammonium radicles $N(C_2H_5)_4$, etc., are not
known in the free state.

A question has at different times been raised regarding
the constitution of ammonium compounds.   It seems, how-
ever, to be now definitely admitted that they contain pentad
nitrogen, ammonium chloride being represented graphi-
cally by the formula :

$$\begin{array}{ccc} H & & H \\ & \diagdown\;\diagup & \\ & N & \\ H\diagup & \big| \diagdown & H \\ & Cl & \end{array}$$
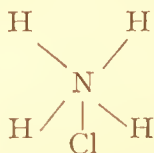
and other ammonium compounds in a corresponding
manner.   Experiment has recently been brought to bear
on the subject in the following manner :

Methyl-triethyl ammonium chloride may be represented
either as an ammonium compound,

$$\begin{array}{ccc} C_2H_5 & & C_2H_5 \\ & \diagdown\;\diagup & \\ & N & \\ \diagup & \big| \diagdown & \\ C_2H_5 & Cl & CH_3 \end{array}$$
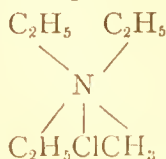
or, as formed on the type of sal-ammoniac, regarded as ammonia hydrochloride $NH_3.HCl$. If the latter view is correct, there ought to be two isomeric compounds having the formulæ

$$N(C_2H_5)_3.CH_3Cl \text{ and } N(C_2H_5)_2(CH_3).C_2H_5Cl.$$
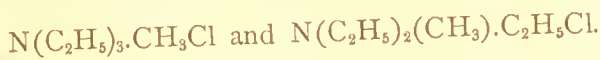
It is found, however, that the result of bringing together triethylamine and methyl chloride, is a body identical in every respect with the product obtained by combining methyl-diethylamine with ethyl chloride.

According to the ammonium formula, which these results tend to support, each radicle is in the same position with respect to the nitrogen, and no isomerism is possible.

Concerning the formation of salammoniac, however, it has been justly remarked, that if we adopt the formula $N^v(H_4Cl')$, it is difficult to explain why, in the combination of hydrochloric acid and ammonia, the chlorine should be represented as leaving the hydrogen, for which it has great attraction, in order to link itself with nitrogen, for which it appears to have little attraction.
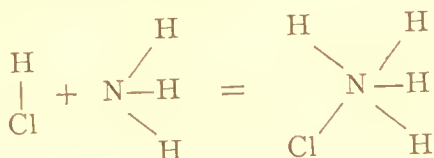
The truth is probably this, that it is the hydrogen of the ammonia, and not the nitrogen, which attracts the chlorine. But this is only one of many cases which show how incompetent are all existing systems of formulæ to represent adequately the essential nature of bodies and the chemical changes they undergo.

Phosphines, *Arsines*, *Stibines*.—By replacing the hydrogen of phosphoretted, arsenetted, and antimonetted hydrogen by hydrocarbon groups, extensive series of bases are obtained, which have received the above names, and, save

for their extreme oxidability, agree in general characters
with the compound ammonias.

Amides.—When the hydrogen of ammonia is replaced by
oxidised or other negative radicles, compounds called
amides are formed. These bodies are, generally speaking,
neutral, though some which contain the radicles of weak
acids are still capable of entering into combination with
acids, and a few are even very decidedly basic ; urea or
carbamide, $CO\,(NH_2)_2$ for example.

On the other hand, some of the amides derived from
polybasic acids are themselves acid bodies. This has been
already referred to (Acids, p. 244).

The general formulæ of amides correspond with those of
amines, and they may be classified into primary, secondary,
and tertiary monamides, diamides, and triamides, and, sub-
stituting negative R or R for R in the formulæ given on
p. 253, they may be tabulated in the same way as the amines.
One slight addition is necessary. Monamines containing
bivalent radicles are not known, but monamides in which
two atoms of hydrogen are replaced by one bivalent acid
radicle, are known under the name imides.

<div style="text-align:center">

Cyanic acid or Carbimide.   Succinimide.

$N \begin{cases} (CO)'' \\ H \end{cases}$ $N \begin{cases} (C_4H_4O_2)'' \\ H \end{cases}$

</div>
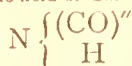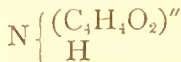
Tertiary derivatives of ammonia, called nitriles or cyanides,
are known in which the three atoms of hydrogen are replaced
by trivalent hydrocarbon groups. We have for example,

<div style="text-align:center">

Formonitrile   Acetonitrile   Benzonitrile

$N(CH)'''$ $N(C_2H_3)'''$ $N(C_7H_5)'''$

or Hydrogen cyanide.   or Methyl cyanide.   or Phenyl cyanide.

</div>

These bodies are not basic, and are decomposed, like all
amides, by boiling with alkalis. Ammonia is evolved, and
a salt formed corresponding with the acid from the ammo-
nium salt of which they were derived by dehydration. Not-
withstanding, therefore, that the replacing radicle contains

no oxygen, these bodies should be ranked with the amides. The isocyanides (pp. 157 and 192) are basic, and are therefore called carb*amines*.

The residual hydrogen of primary and secondary amides may be replaced by positive or hydrocarbon radicles. Compounds intermediate between amines and amides then result. The following are examples:—
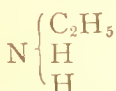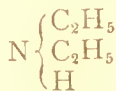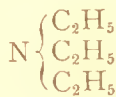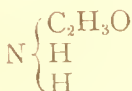
$$N \begin{cases} C_2H_5 \\ H \\ H \end{cases}$$

Ethylamine.

$$N \begin{cases} C_2H_5 \\ C_2H_5 \\ H \end{cases}$$

Diethylamine.

$$N \begin{cases} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{cases}$$

Triethylamine.

$$N \begin{cases} C_2H_3O \\ H \\ H \end{cases}$$

Acetamide.

$$N \begin{cases} C_2H_3O \\ C_2H_3O \\ H \end{cases}$$

Diacetamide.

$$N \begin{cases} C_2H_3O \\ C_2H_3O \\ C_2H_3O \end{cases}$$

Triacetamide.

$$N \begin{cases} C_2H_3O \\ C_2H_5 \\ C_2H_5 \end{cases}$$

Diethylacetamide.

$$N \begin{cases} C_2H_3O \\ C_2H_3O \\ C_2H_5 \end{cases}$$

Ethyldiacetamide.

$$N \begin{cases} C_2H_3O \\ C_2H_5 \\ H \end{cases}$$
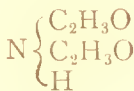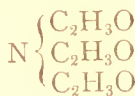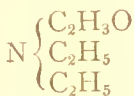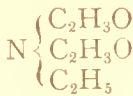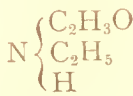
Ethylacetamide.

CHAPTER XXVI.

CARBON COMPOUNDS.

BODIES having the same chemical functions, and constituting a series in which, between any two contiguous terms, there is a constant difference of CH_2, are said to be homologous, and the series is a *homologous series*. Relations of a like nature have not hitherto been observed among the compounds of any element but carbon.[*] This peculiarity

* And probably silicon. Unless, indeed, we choose to regard such a pair of compounds as tetrachloride and sesquichloride of manganese, $MnCl_4$, Mn_2Cl_6, as the two first terms of a series $Mn_n Cl_{2n+2}$, the higher members of which are unknown.

seems to be connected with a special faculty with which carbon atoms appear to be endowed, the power, namely, of uniting with one another without the intervention of any other element. Thus a very large number of different compounds containing carbon and hydrogen, either alone or associated with oxygen or nitrogen, have already been produced, and a still larger number of possible combinations of carbon is indicated by theory.

Notwithstanding that, by reason of their composition being unknown or their reactions imperfectly studied, a considerable number of carbon compounds remain unclassified, it has been found that nearly all well-known compounds range themselves naturally in one or other of the following classes :—

I. HYDROCARBONS AND HALOID DERIVATIVES.

Some hundreds of compounds consisting only of carbon and hydrogen have been described, but no such compound is known of which two volumes of the vapour contain a larger quantity of hydrogen than is represented by the general formula C_nH_{2n+2}. This fact is explained by the following hypothesis. A single atom of carbon has four units of atomicity, each of which is capable of being saturated by one atom of hydrogen. We thus arrive at the formula,

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H}-\text{C}-\text{H} \\
| \\
\text{H}
\end{array}
$$
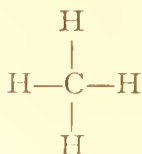
which represents marsh gas. This body is absolutely saturated, and nothing will induce it to take up additional elements of any kind, except on condition of removing one or more of its hydrogen atoms. If, now, we imagine another atom of carbon similarly loaded with hydrogen presented to it, the only mode in which they can unite together is by

the severance of an atom of hydrogen from each group, as represented in the following diagram :—

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H—C— H} \\
| \\
\text{H}
\end{array}
\qquad\qquad
\begin{array}{c}
\text{H} \\
| \\
\text{H—C—H} \\
| \\
\text{H}
\end{array}
$$

or

$$
\begin{array}{cc}
\text{H} & \text{H} \\
| & | \\
\text{H—C—C—H} \\
| & | \\
\text{H} & \text{H}
\end{array}
$$
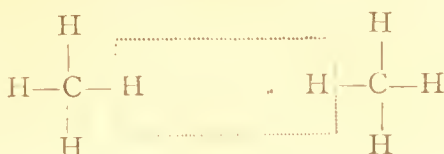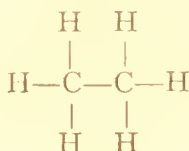
The same process may be repeated *ad infinitum*. The number of hydrogen atoms in the first term of the series being 4, in the second $2 \times 4 - 2$, in the third $3 \times 4 - 4$, in the nth term the number will be $4n - (2n - 2)$, or $2n + 2$.

The most important series of hydrocarbons at present known are represented by the following general formulæ :—

Paraffins, or Marsh Gas Series, C_nH_{2n+2}
Olefines, or Olefiant Gas Series, C_nH_{2n}
Acetylene Series, C_nH_{2n-2}
Terpene Series, C_nH_{2n-4}
The lowest known term of the terpene series contains C_{10}.
Benzene series, C_nH_{2n-6}.

The lowest term of this series contains C_6, it is called benzene, and is represented by the following graphic formula :

$$
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{C—C} \\
\text{//} \qquad \text{\\} \\
\text{HC} \qquad \text{CH} \\
\text{\\} \qquad \text{/} \\
\text{C = C} \\
\text{H} \qquad \text{H}
\end{array}
$$
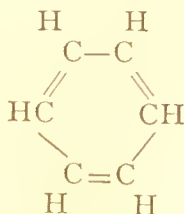
It gives rise to a large number of substitution derivatives, among which occur many isomerides. The differences observed among these compounds are attributed to the assumption of different relative positions by the replacing radicles.

Hydrocarbons differ very much in their physical properties, and in the nature of the reactions to which they lend themselves. This, of course, depends upon the series to which they belong, but taking any one series, such as the paraffins, it is found that a regular gradation may be traced in the physical properties of the several members of the series, passing from the lowest to the highest terms.

Thus the first three members of the paraffin series are gaseous, methane having indeed resisted all attempts to liquefy it; the succeeding members are liquid, but become less and less volatile,* and at the same time more dense and viscid, till among the highest members of the series we come to crystalline solid bodies, which are vola- tilisable only at such high temperatures that they cannot be distilled without extensive decomposition. In proportion as we ascend the series the percentage of hydrogen rapidly decreases, and this, together with the diminished mobility of the body, may perhaps account for the comparative indif- ference to chemical reagents exhibited by the higher mem- bers.

A corresponding seriation of properties, both physical and chemical, is observed in other groups of bodies related to one another in a similar manner.

2. ALCOHOLS.

These bodies may be regarded as hydrates of hydro- carbon radicles, considering that in their most pro- minent and characteristic reactions, they resemble water

* See Chapter IV., p. 23.

and the hydrates of the metals. They are either liquids or solids, and they are obtained in a variety of processes; but the ethylic, or common alcohol of fermentation was the first studied, and is the best known of the class. Taking it as the representative of alcohols in general, we may record the following as its characteristic reactions :

(*a*). By the action of an alkali metal it loses hydrogen.

$$C_2H_5HO \quad + \quad K \quad = \quad C_2H_5KO \quad + \quad H.$$
Alcohol. Potassic ethylate.
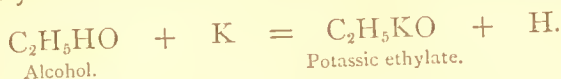
(*b*) By the action of acids or acid anhydrides, it is converted into salts, called compound ethers, *e.g.* :

$$C_2H_5HO \quad + \quad HCl \quad = \quad C_2H_5Cl \quad + \quad H_2O.$$
Alcohol. Ethyl chloride.

$$C_2H_5HO \quad + \quad H_2SO_4 = \quad C_2H_5HSO_4 \quad + \quad H_2O.$$
Alcohol. Ethyl-hydrogen sulphate.

$$2C_2H_5HO \quad + \quad (C_2H_3O)_2O \quad = \quad 2C_2H_5C_2H_3O_2 \quad + \quad H_2O.$$
Alcohol. Acetic anhydride. Ethyl acetate.
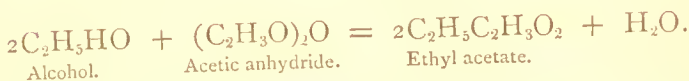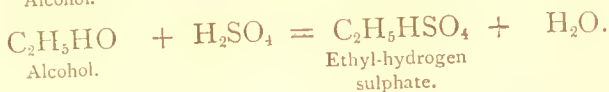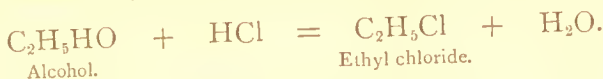
(*c*) The alcohol is reproduced from these salts by the action of alkalies :

$$C_2H_5Cl \quad + \quad KHO \quad = \quad C_2H_5HO \quad + \quad KCl.$$

Alcohols are divisible into several classes, according to the number of hydroxyl groups in the molecule. Monohydric alcohols yield one saline derivative or compound ether, dihydric alcohols give two, trihydric alcohols give three such compounds, and so on.

But they are also divisible into several other groups, which are characterised by their behaviour when submitted to oxidation.

Primary alcohols, when oxidised, lose hydrogen, and yield bodies which are called aldehyds; thus common alcohol loses two atoms of hydrogen :

$$C_2H_6O \quad + \quad O \quad = \quad C_2H_4O \quad + \quad OH_2.$$
Alcohol. Aldehyd.
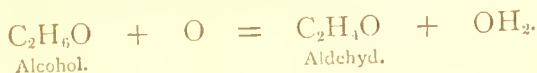
Secondary alcohols, under the influence of similar re-agents, yield ketones; for example :

$$C_3H_8O \quad + \quad O \quad = \quad C_3H_6O \quad + \quad OH_2.$$
Isopropylic alcohol.   Acetone.

Tertiary alcohols, when oxidised, break up into a mixture of acids, each containing a smaller number of carbon atoms than the alcohol.

These differences are accounted for by the following hypothesis. The generating hydrocarbon is supposed to be marsh gas or methane, and by the replacement of one of its hydrogen atoms by hydroxyl, an alcohol called methylic alcohol is formed.

Methane.   Methylic hydrate or alcohol.

$$C \begin{cases} H \\ H \\ H \\ H \end{cases} \qquad\qquad C \begin{cases} H \\ H \\ H \\ OH \end{cases}$$
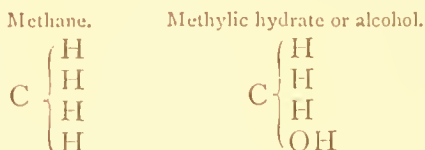
By replacing another atom of hydrogen by a hydrocarbon group, one of the higher homologues of methylic alcohol is produced. Now, so long as the replacement is effected in such a manner as to leave two of the hydrogen atoms of the marsh gas type undisturbed, the product is a primary alcohol, which by the substitution of an atom of oxygen for these two atoms of hydrogen, is capable of giving rise to an aldehyd.

Primary alcohols.   Aldehyds.

$$C \begin{cases} CH_3 \\ H \\ H \\ OH \end{cases} \quad C \begin{cases} C(CH_3)H_2 \\ H \\ H \\ OH \end{cases} \text{ etc.} \qquad C \begin{cases} CH_3 \\ O \\ H \end{cases} \quad C \begin{cases} C(CH_3)H_2 \\ O \\ H \end{cases} \text{ etc.}$$
Ethylic.   Propylic.   Acetic.   Propionic.
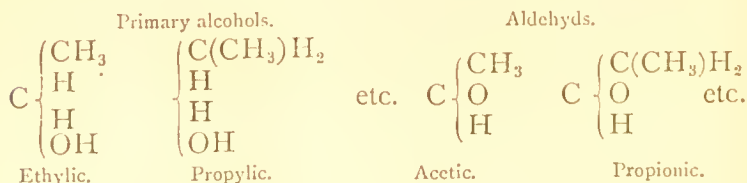
If, however, the second step in the process of replace-ment affects one of these typical hydrogen atoms, then a secondary alcohol is produced, and this body cannot take in oxygen in the same manner as the primary alcohols, but

it may lose two atoms of hydrogen, as represented by the following formula :

Secondary alcohol.

$$C \begin{cases} CH_3 \\ CH_3 \\ H \\ OH \end{cases}$$

Propylic.

Ketone.

$$C \begin{cases} CH_3 \\ CH_3 \\ O'' \end{cases}$$
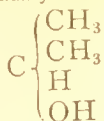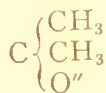
Acetone or dimethyl-ketone.

Lastly, the tertiary alcohols are generated in the same manner by the replacement of the last atom of hydrogen originally belonging to the type, thus :

Tertiary alcohols.

$$C \begin{cases} CH_3 \\ CH_3 \\ CH_3 \\ OH \end{cases}$$

Butylic.
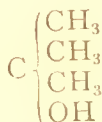
$$C \begin{cases} C(CH_3)H_2 \\ CH_3 \\ CH_3 \\ OH \end{cases} \quad \text{etc.}$$
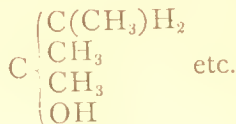
Amylic.

It is obvious from this that, although a primary alcohol may contain one or two atoms of carbon, no secondary alcohol containing less than three atoms, and no tertiary alcohol containing less than four atoms of carbon in the molecule can exist.

Another class of alcohols, called phenols, is also known. These agree to some extent with secondary alcohols, inasmuch as they yield no aldehyd by oxidation, but furnish compounds containing the same number of carbon atoms as themselves. These substances, however, are not ketones. They are called quinones.

No phenol is known to contain fewer than six carbon atoms in the molecule. They are regarded as derived from benzene or some analogous hydrocarbon. The best known phenol is the body which usually goes by that name among chemists, or, in common parlance, carbolic acid, C_6H_5OH. In accordance with the formula, it might also be called phenyl hydrate, or phenyl alcohol. It differs from ordinary alcohols in yielding a great number of substitution derivatives, most of which exhibit well-marked acid properties.

Thus the trinitrophenol is commonly called picric, or trinitrophenic acid. The following are the formulæ of its chloro and nitro derivatives :

Monochlorophenol	.	$C_6H_4Cl.OH$
Dichlorophenol	.	$C_6H_3Cl_2.OH$
Trichlorophenol	.	$C_6H_2Cl_3.OH$
Pentachlorophenol	.	$C_6Cl_5.OH$
Mononitrophenol	.	$C_6H_4(NO_2)\cdot OH$
Dinitrophenol	.	$C_6H_3(NO_2)_2.OH$
Trinitrophenol	.	$C_6H_2(NO_2)_3.OH$

Several isomeric modifications of the mono and di derivatives are known.

3. ETHERS.

These bodies have the same relation to alcohols as the metallic oxides to their hydrates. They are, however, not easily converted into alcohols by the direct action of water, neither are they obtained from alcohols so readily as the metallic oxides from hydrates. The oxides corresponding with the dihydric alcohols seem to undergo this transformation more readily than those belonging to the monohydric alcohols.

The following are some examples of simple and mixed ethers :

$\begin{rcase} CH_3 \\ CH_3 \end{rcase} O$

Methylic oxide or ether.

$\begin{rcase} CH_3 \\ C_2H_5 \end{rcase} O$

Methyl-ethylic oxide or ether.

$\begin{rcase} C_2H_5 \\ C_2H_5 \end{rcase} O$

Ethylic oxide (common ether).

$(C_2H_4)''O$

Ethene oxide or ether.

$(C_3H_5)_2'''O_3$

Glyceryl oxide or ether.

The known ethers are volatile liquids of aromatic odour.

4. ALDEHYDS AND KETONES.

These two classes of compounds are closely related, both as regards their mode of formation, and properties and composition.

Aldehyds are formed by the oxidation of primary alcohols, ketones by the oxidation of secondary alcohols. Thus

common aldehyd results from the removal of two atoms of hydrogen from common (ethylic) alcohol :—

$$C_2H_6O \quad — \quad H_2 \quad = \quad C_2H_4O$$
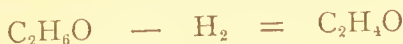
Acetone, the best known of the ketones, stands in the same relation towards isopropylic alcohol :—

$$C_3H_8O \quad — \quad H_2 \quad = \quad C_3H_6O$$

It has already been shown that no secondary alcohol can contain less than three atoms of carbon, and, consequently, there can be no ketone, properly so called, containing less carbon than acetone, C_3H_6O.

The formation of this body by the action of zinc methyl (see *organo-metallic compounds*) on carbonyl chloride shows that it contains two methyl groups united with the carbonyl radicle :—

$$CO\begin{cases}Cl \\ Cl\end{cases} \quad + \quad Zn\begin{cases}CH_3 \\ CH_3\end{cases} \quad = \quad ZnCl_2 \quad + \quad CO\begin{cases}CH_3 \\ CH_3\end{cases}$$

Carbonyl chloride.   Zinc methyl.   Zinc chloride.   Acetone.
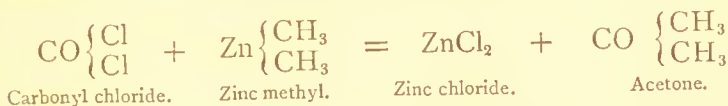
It thus appears that the aldehyds of the monocarbon and dicarbon series may be considered to be homologous with the higher aldehyds on the one hand, and with the ketones on the other. The following formulæ indicate the relationship :—

Formic aldehyd or ketone. $CO\begin{cases}H \\ H\end{cases}$ (gaseous)

Acetic aldehyd or ketone. $CO\begin{cases}H \\ CH_3\end{cases}$ (B.P. 22°)

Aldehyds.	Ketones.
Propionic.	Dimethyl (Acetone).
$CO\begin{cases}H \\ C_2H_5\end{cases}$ (B.P. 48°.5)	$CO\begin{cases}CH_3 \\ CH_3\end{cases}$ (B.P. 56')
Butyric.	Methyl-ethyl.
$CO\begin{cases}H \\ C_3H_7\end{cases}$ (B.P. 75")	$CO\begin{cases}CH_3 \\ C_2H_5\end{cases}$ (B.P. 81°)

Valeric.

$$CO\begin{Bmatrix} H \\ C_4H_9 \end{Bmatrix}(\text{B.P. } 102°)$$

Metameric.

Diethyl.

$$CO\begin{Bmatrix} C_2H_5 \\ C_2H_5 \end{Bmatrix}(\text{B.P. } 100°)$$

Methyl-propyl.

$$CO\begin{Bmatrix} CH_3 \\ C_3H_7 \end{Bmatrix}(\text{B.P. } 101°)$$

Methyl-isopropyl.

$$CO\begin{Bmatrix} CH_3 \\ CH(CH_3)_2 \end{Bmatrix}(\text{B.P. } 93°)$$
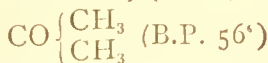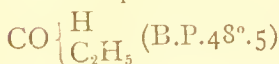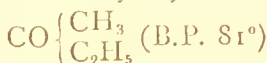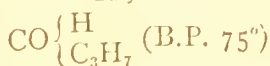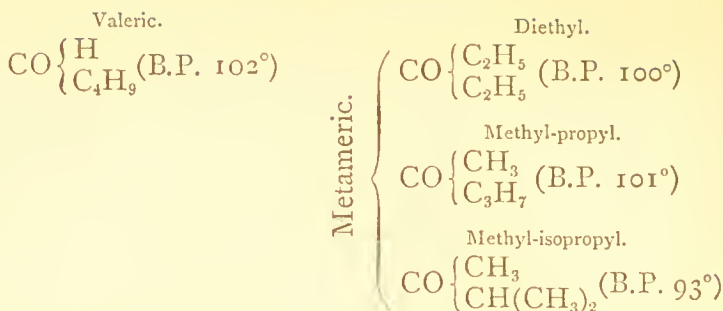
From the existence of such intimate relations between these two classes of compounds, it is not extraordinary that in many of their properties there should be considerable resemblance between them.

(*a*) By the action of nascent hydrogen, generated by the action of sodium amalgam in the presence of water, aldehyds and ketones are converted into the corresponding alcohols, *e.g.* :—

$$\underset{\text{Acetic aldehyd.}}{C_2H_4O} + H_2 = \underset{\text{Ethyl alcohol.}}{C_2H_6O}$$

$$\underset{\text{Acetone.}}{C_3H_6O} + H_2 = \underset{\text{Isopropyl alcohol:}}{C_3H_8O}$$
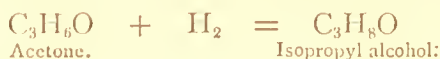
(*b*) All aldehyds and many ketones combine with the acid sulphite of sodium, forming crystallisable compounds, which yield up the aldehyd or ketone again by treatment with an acid or an alkaline carbonate.

(*c*) By boiling with hydrocyanic acid and hydrochloric acid, aldehyds and ketones are converted into acids containing in the molecule one more atom of carbon than themselves. For example, common aldehyd is converted into one form of lactic acid.

$$CO\begin{Bmatrix} CH_3 \\ H \end{Bmatrix} + HCN + 2H_2O + HCl$$
Aldehyd.   Hydrocyanic acid.

$$= \begin{Bmatrix} CH_3 \\ CH{\diagdown\diagup}^{OH}_{}\diagdown CO.OH \end{Bmatrix} + NH_4Cl$$
Ethidene lactic acid.   Ammonium chloride.
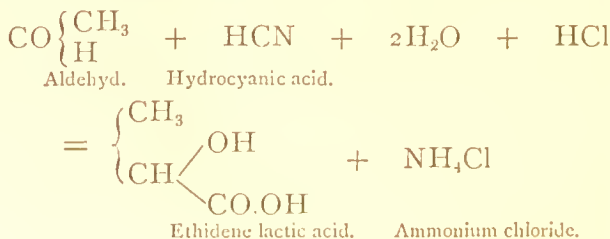
Acetone is converted by a similar process into a homologue of lactic acid,

$$CO\begin{cases}CH_3 \\ CH_3\end{cases} + HCN + 2H_2O + HCl$$

Acetone. Hydrocyanic acid.

$$= \begin{cases} CH_3 \\ C \diagdown \begin{matrix} CH_3 \\ OH \\ CO.OH \end{matrix} \end{cases} + NH_4Cl$$

Acetonic or oxybutyric acid. Ammonium chloride.
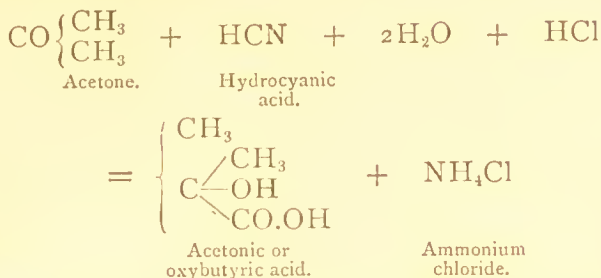
Notwithstanding these various points of resemblance, ketones are sharply distinguished from aldehyds by the action of agents of oxidation.

An aldehyd is always converted by oxidation into an acid containing the same number of atoms of carbon.

A ketone, on the contrary, is much more difficult to oxidise, and is then broken up into a mixture of acids, each containing a smaller number of carbon atoms. This oxidation proceeds according to a definite law.

5. ACIDS.

Every carbon acid may be considered to have been derived from an alcohol by the substitution of an atom of oxygen for two atoms of hydrogen.

Monohydric alcohols yield monobasic acids. For example, ethylic alcohol yields acetic acid :—

$$C_2H_5.OH. - H_2 + O = C_2H_3O.OH$$

Ethyl alcohol. Acetic acid.

Dihydric alcohols may yield either monobasic or dibasic acids. Ethene alcohol or glycol, for example, may be converted into monobasic glycollic or dibasic oxalic acid, thus:

$$C_2H_4(OH)_2 - H_2 + O = C_2H_2O(OH)_2$$

Ethene alcohol. Glycollic acid.

$$C_2H_4(OH)_2 - 2H_2 + O_2 = C_2O_2(HO)$$

Ethene alcohol. Oxalic acid.
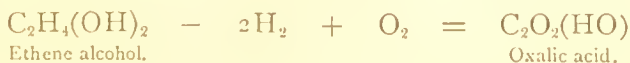
Trihydric alcohols may yield theoretically either mono-basic, dibasic, or tribasic acids. Very few of these deriva-tives, however, are actually known. Thus glycerine, which is a trihydric alcohol, yields, upon oxidation, only one acid containing the same number of carbon atoms. This glyceric acid is monobasic.

$$C_3H_5(OH)_3 \; - \; H_2 \; + \; O \; = \; C_3H_3O(OH)_3$$
Glycerine.   Glyceric acid.

A large number of acids are known, the alcohols corre-sponding to which·have not yet been discovered.

Acids, however, may be generated by an entirely different process from alcohols containing one atom less carbon. This process is interesting, because it serves to indicate the general constitution of carbon acids.

Starting from methyl alcohol, $CH_3 \cdot OH$, for example, we may convert this body into the corresponding cyanide $CH_3 \cdot CN$. When boiled with caustic potash this com-pound undergoes decomposition, ammonia is evolved, and the potassium salt of acetic acid is generated.

$$CH_3 \cdot CN \; +\!\!\cdot \; KHO \; + \; H_2O \; = \; CH_3 \cdot CO(OK) \; + \; NH_3$$
Methyl cyanide.   Potash.   Water.   Potasium acetate.   Ammonia.
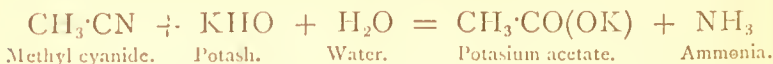
Or leaving the potassium out of sight, the reaction may be represented as follows :—

$$CH_3 \cdot CN \; + \; 2H_2O \; = \; CH_3 \cdot CO(OH) \; + \; NH_3$$

From this it appears that the acid is generated by the substitution of $O'' + (OH)'$ for the N''' of the cyanide. Acetic acid then consists of a methyl group, CH_3, com-bined with a *carboxyl* group, $CO \cdot OH$. Now methylic alcohol is monohydric, and therefore is capable of yielding one cyanide and no more. Consequently, from methylic alcohol only one derivative containing the carboxyl group can be formed, and that derivative is a monobasic acid. In a similar manner it is found that, by decomposing the cyanide of a bivalent alcohol radicle by boiling alkali, a

bibasic acid is produced, whilst the cyanide of a trivalent radicle yields by the same process a tribasic acid. Setting down examples of compounds generated in this way, we find that they all contain the group CO.OH, once, twice, or three times in the molecule, according to the saturating power of the acid.

Monobasic acetic acid.	Dibasic succinic acid.*	Tribasic tricarballylic acid.
$CH_3 \cdot CO(OH)$	$C_2H_4 \begin{cases} CO(OH) \\ CO(OH) \end{cases}$	$C_3H_5 \begin{cases} CO(OH) \\ CO(OH) \\ CO(OH) \end{cases}$
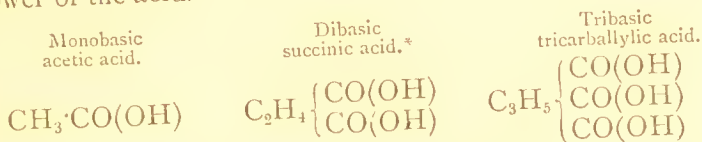
This carboxyl group then is contained in a very large number of carbon acids, and its presence seems to be intimately connected with the development of the acid character in these compounds. We have seen (Phenols, p. 263) that the halogens and the nitroxyl group $(NO_2)'$ when substituted for hydrogen in certain oxidised bodies also constitute acidifying agents, but the presence of these radicles in varying quantities does not affect the basicity of the resulting acid; whereas it seems to have been established that an acid which contains the carboxyl, $CO(OH)$, group n times is n basic.

Carbon acids, when submitted to the action of the halogens, yield a great many substitution derivatives, such as the following chlorinated compounds, which are obtained from acetic acid :—

> Monochloracetic acid $CH_2Cl \cdot COOH$
> Dichloracetic acid $CHCl_2 \cdot COOH$
> Trichloracetic acid $CCl_3 \cdot COOH$
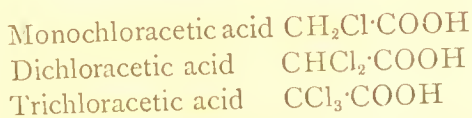
But here the process of substitution stops, the hydrogen of the carboxyl being replaceable only by metallic or positive radicles, and not by negative bodies.

The metallic salts, amides, anhydrides, and chlorides derived from a carbon acid, correspond in number, mode of

* See molecular weights, Chapter XVI. p. 126.

formation, and general properties with the same derivatives
of mineral acids.*

6. BASIC DERIVATIVES OF AMMONIA.

The constitution and general properties of these bodies
have already been discussed. (Amines, p. 252.)

The "alkaloids," quinine, morphine, strychnine, and
many others which are obtained from various plants, and
constitute important medicinal agents, are referable to this
type. They are for the most part tertiary amines.

7. COMPOUND ETHERS OR ETHEREAL SALTS.

The most general method for the formation of these com-
pounds consists in heating together an acid and an alcohol.
A double decomposition ensues; water is formed, together
with the ethereal salt ; so that the reaction is exactly
parallel with the change which occurs when an ordinary
acid and basic oxide are brought into contact. The fol-
lowing equations, for example, are strictly comparable :—

$$KHO + HNO_3 = KNO_3 + H_2O$$
Basic oxide.   Acid.   Salt.   Water.

$$C_2H_5.HO + HC_2H_3O_2 = C_2H_5.C_2H_3O_2 + H_2O$$
Alcohol.   Acid.   Ethereal Salt.   Water.
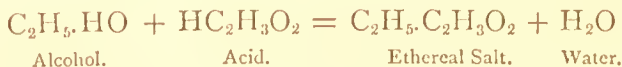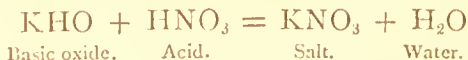
Compound ethers also imitate metallic salts in their
general reactions. Thus they are decomposed by acids, by
alkalies, and by water in precisely the same manner. They
differ from metallic salts, however, in many physical cha-
racters, being for the most part volatile liquids of aromatic
odour, and very slightly soluble in water, though generally
miscible with alcohol in all proportions. Comparatively
few are crystallisable. Among the most interesting examples

* Pp. 242 to 246.

of crystallisable ethereal salts are the constituents of the natural fats :—

Palmitin
or glyceric palmitate

$$\left. \begin{array}{l} C_{15}H_{31}.CO.O \diagdown \\ C_{15}H_{31}.CO.O \!\!-\!\! (C_3H_5)''' \\ C_{15}H_{31}.CO.O \diagup \end{array} \right.$$

and

Stearine or
glyceric stearate

$$\left. \begin{array}{l} C_{17}H_{35}.CO.O \diagdown \\ C_{17}H_{35}.CO.O \!\!-\!\! (C_3H_5)''' \\ C_{17}H_{35}.CO.O \diagup \end{array} \right.$$
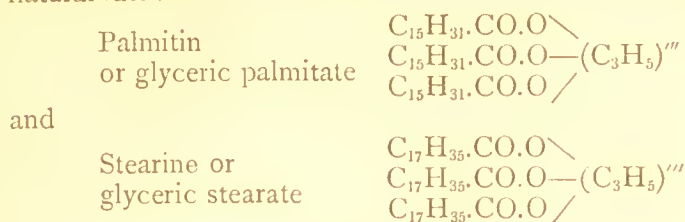
8. ORGANO-METALLIC COMPOUNDS.

These are compounds of metals or metalloids with hydrocarbon radicles. They are volatile, very oxidisable, and generally heavy liquids. The zinc-ethyl compound was first obtained. It is a colourless liquid, boiling at 118°, and spontaneously inflammable when thrown into the air. It is instantly decomposed by water, and when submitted to the action of successive small quantities of oxygen, it yields two oxidised compounds, thus :—

Zinc ethide.   Zinc ethyl-ethylate.   Zinc ethylate.

$$Zn \begin{cases} C_2H_5 \\ C_2H_5 \end{cases} \qquad Zn \begin{cases} C_2H_5 \\ OC_2H_5 \end{cases} \qquad Zn \begin{cases} OC_2H_5 \\ OC_2H_5 \end{cases}$$
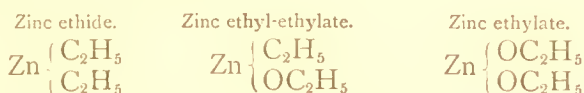
Iodine removes from it half and then the whole of the ethyl, according to these equations :—

$$Zn(C_2H_5)_2 + I_2 \quad = \quad Zn(C_2H_5)I \quad + \quad C_2H_5I$$
<div align="center">Zinc ethiodide.   Ethyl iodide.</div>

$$Zn(C_2H_5)I + I_2 \quad = \quad ZnI_2 \quad + \quad C_2H_5I$$
<div align="center">Zinc iodide.   Ethyl iodide.</div>
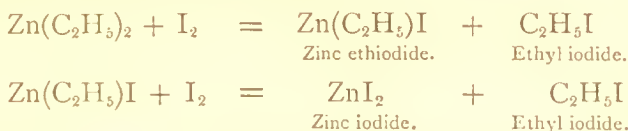
The existence of these compounds furnishes conclusive testimony of the diadic character of the zinc atom, and in other cases similar evidence, of great value in settling questions relating to atomicity and atomic weight, has been obtained by the study of these compounds.

The following are the formulæ of some of the most interesting organo-metallic bodies. It will be noticed that they are constituted in the same way as the chlorides and

oxides of the same hydrocarbon radicles, the special peculiarities of the organo-metallic bodies being due to the unoxidised condition of the metals they contain.

The vapour densities of all these compounds are normal, so that each formula represents two volumes of vapour.

Ethyl chloride or chlorine ethide	. .	$\overset{\prime}{C}l - C_2H_5$
Ethyl oxide or oxygen ethide	. .	$\overset{\prime\prime}{O}\begin{cases}C_2H_5 \\ C_2H_5\end{cases}$
Boron ethide	. .	$\overset{\prime\prime\prime}{B}\begin{cases}C_2H_5 \\ C_2H_5 \\ C_2H_5\end{cases}$
Silicon ethide	. .	$\overset{\text{IV}}{Si}\begin{cases}C_2H_5 \\ C_2H_5 \\ C_2H_5 \\ C_2H_5\end{cases}$
Trimethyl arsine . or arsenious trimethide	. .	$\overset{\prime\prime\prime}{As}\begin{cases}CH_3 \\ CH_3 \\ CH_3\end{cases}$
Diarsenious tetramethide (kakodyl)	.	$\begin{cases}\overset{\prime\prime\prime}{As}(CH_3)_2 \\ \overset{\prime\prime\prime}{As}(CH_3)_2\end{cases}$
Trimethyl stibine or antimonious trimethide	. .	$\overset{\prime\prime\prime}{Sb}\begin{cases}CH_3 \\ CH_3 \\ CH_3\end{cases}$
Triethyl bismuthine or bismuthous triethide	.	$\overset{\prime\prime\prime}{Bi}\begin{cases}C_2H_5 \\ C_2H_5 \\ C_2H_5\end{cases}$
Zinc ethide	. .	$Zn\begin{cases}C_2H_5 \\ C_2H_5\end{cases}$
Mercuric ethide .	. .	$Hg\begin{cases}C_2H_5 \\ C_2H_5\end{cases}$
Stannous ethide .	. .	$\overset{\prime\prime}{Sn}\begin{cases}C_2H_5 \\ C_2H_5\end{cases}$

Stannic ethide .   .   . $\mathrm{Sn^{iv}} \begin{cases} \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \end{cases}$

Plumbic ethide .   .   . $\mathrm{Pb^{iv}} \begin{cases} \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \end{cases}$

EXERCISES ON SECTION V.

1. Write down the formulæ of all the possible silver salts of the following acids :—

$\mathrm{HClO_3}$, $\mathrm{HClO_4}$, $\mathrm{H_2SO_4}$, $\mathrm{H_3PO_4}$, $\mathrm{H_4SiO_4}$, $\mathrm{H_2SO_3}$, $\mathrm{H_3PO_3}$.

2. Write down the formulæ for all the chlorides and amides theoretically derivable from the following acids :—

$\mathrm{HNO_3}$, $\mathrm{H_2SO_4}$, $\mathrm{H_4P_2O_7}$, $\mathrm{HC_7H_5O_2}$ (benzoic acid, monobasic).

3. Write the constitutional formulæ of Nordhausen sulphuric acid, $\mathrm{H_2S_2O_7}$, of permanganic acid, $\mathrm{H_2Mn_2O^8}$, and of chromic acid, $\mathrm{H_2CrO_4}$, assuming sulphur, manganese, and chromium hexad.

4. Write down the formulæ for the possible anhydrides derived from orthosulphuric acid, $\mathrm{S(OH)_6}$, by successive stages of dehydration.

5. Give the formulæ for the anhydrides corresponding with sulphuric acid, $\mathrm{H_2SO_4}$, phosphoric acid, $\mathrm{H_3PO_4}$, pyrophosphoric acid, $\mathrm{H_4P_2O^7}$, nitric acid, $\mathrm{HNO_3}$, nitrous acid, $\mathrm{HNO_2}$, hyponitrous acid, HNO, theiosulphuric acid, $\mathrm{H_2S_2O_3}$, chloric acid, $\mathrm{HClO_3}$, perchloric acid, $\mathrm{HClO_4}$, and acetic acid, $\mathrm{HC_2H_3O_2}$, pointing out those which are actually known.

6. Give concise definitions of the terms *acid*, *base*, *salt*, with examples of their characteristic properties drawn from your own experience.

7. How would you explain the terms acid, and neutral salt ?   Give examples.

8. A number of salts having the general formula $\mathrm{M'HSO_2}$ were called by the discoverer hydrosulphites.   What name should they bear according to the rules laid down in Chapter XII. ?   Write the graphic formulæ for these bodies, and mention compounds which are similarly constituted.

9. Complete the following equations, adding the name to each formula :—

$$HNO_3 + PbO =$$
$$HNO_3 + NH_3 =$$
$$H_2SO_4 + KHO =$$
$$H_2SO_4 + PCl_5 =$$
$$(NH_4)_2SO_4 - 2H_2O =$$
$$(NH_4)HSO_4 - H_2O =$$
$$(NH_4)_2CO_3 - H_2O =$$
$$(NH_4)_2CO_3 - 2H_2O =$$
$$C_2H_3OCl + OH_2 =$$
$$Ca(HO)_2 - H_2O =$$
$$CaCl_2 + Na_2CO_3 -$$
$$CaCO_3 + 2NH_4Cl =$$
$$NH_3 + C_2H_5I =$$
$$NH_2C_2H_5 + C_2H_5I =$$
$$NH(C_2H_5)_2 + C_2H_5I =$$
$$N(C_2H_5)_3 + C_2H_5I =$$
$$N(C_2H_5)_4I + AgHO =$$
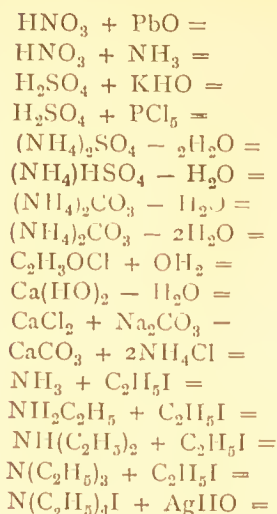
10. Give reasons in favour of each of these formulæ for sal-ammoniac :—

$$NH_3 \cdot HCl$$
$$NH_4Cl$$
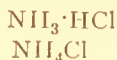
11. To which class of compounds would you refer the following substances :—

Caustic potash, KHO ; lime, CaO ; nitrous oxide, N_2O ; nitrogen trioxide, N_2O_3 ; ferric oxide, Fe_2O_3 ; chromium trioxide, CrO_3 ; wood spirit, $CH_3 \cdot OH$; glycerine, $C_3H_5(OH)_3$; urea, $CO(NH_2)_2$.

12. Accepting the formula HCl for hydrochloric acid, what facts determine the choice of the formula $H_2C_2O_4$ for oxalic acid ?

13. How far do the following compounds agree with definitions of the terms acid, base, salt ? Give sufficient reasons in each case.

Chlorides of hydrogen, potassium, aluminium, phosphorus, sulphur ; oxides of hydrogen, potassium, carbon ; hydrates of potassium, aluminium, arsenic, silicon.

14. Define the term hydrate. Classify the following compounds :—

$$Cl_2.\text{10}H_2O - KHO - H_3AlO_3 - C_2H_5OH.$$
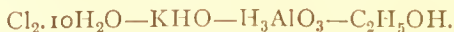
15. Write the constitutional formula of urea, and of the compound with which it is isomeric.

16. How many litres of marsh gas would be equal in weight to 25 litres of ethene ?

17. Benzoate of silver has the formula $C_7H_5AgO_2$. Calculate its percentage composition, also the weight of silver contained in ·5736 gram of this salt.

18. From the formulæ HBr, H_2S, CCl_4, NH_4Cl, H_2SO_4, state the quantivalence of the symbols Br, S, C, N, and S, giving your reasons in each case.

19. Name and classify the following compounds :—

CH_4, $CHCl_3$, C_2H_6

C_2H_5Cl, $\left.\begin{array}{c}C_2H_5\\C_2H_5\end{array}\right\}O$, $\left.\begin{array}{c}C_2H_5\\C_2H_5\end{array}\right\}Zn$,

$\left.\begin{array}{c}C_2H_5\\H_2\end{array}\right\}N$, $\left.\begin{array}{c}CH_3\\(C_2H_5)_2\end{array}\right\}N$, $\left.\begin{array}{c}CH_3\\C_2H_3O\end{array}\right\}O$
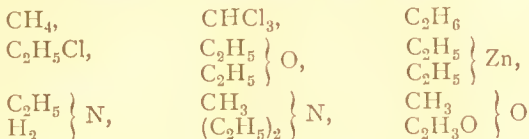
20. Assign a formula to a body containing C26·6, H2·2, and O71·1 per cent.

21. How would you prove that the formula of marsh gas is CH_4? Also, how could you show that ethylene contains twice as much carbon?

22. Give reasons for representing oxalic acid as $C_2H_2O_4$, not CHO_2; acetic acid as $C_2H_4O_2$, not CH_2O; ethylene as C_2H_4, not CH_2.

23. By what experiments could you prove that the molecule of benzene is correctly represented by the formula C_6H_6 not C_3H_3?

24. A body having the composition $C_5H_{12}O$ is an alcohol. Express by equations the probable action upon it of acetic acid, oxalic acid, and oxidising agents.

25. The compound C_4H_8O is either an aldehyd or a ketone. How would you recognise its true character? Write out the constitutional formula of the aldehyd and ketone of this composition, and indicate the constitution of any metameric modification that may exist.

26. Dissect the crude formula $C7H_{14}O_2$, showing the nature of the several metameric compounds which it may represent.

27. In respect of what properties may you regard alcohols as water molecules in which hydrogen has been replaced by hydrocarbon radicles? Illustrate by reference to common alcohol, C_2H_5OH.

28. The ethylic series of monohydric alcohols are represented by the general formula—

$$CnH_{2n+1}OH.$$
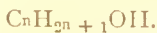
Write out the formula for the corresponding aldehyds, acids, and acetic derivatives (acetates).

29. How many acids could be derived from the alcohol—

$$\begin{array}{c}CH_2·OH\\CH_2·OH,\end{array}$$
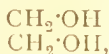
and what would be their formulæ?

30. Carbolic acid is sometimes called phenylic alcohol. In what respects do its alcoholic properties differ from those of the alcohols of the ethylic series, $C_nH_{2n+2}O$?

31. Complete these equations :—

$$CH_3 \cdot CO(OH + PCl_5 =$$
$$CH_3 \cdot OH + HCl =$$
$$\left. \begin{array}{l} CH_3 \\ CH_3 \end{array} \right\} O + 2HCl =$$
$$2CH_3 \cdot CO(OH) + Ag_2O =$$
$$\left. \begin{array}{l} CH_3 \cdot OH + C_2H_5O \\ HO \end{array} \right\} SO_2 =$$
$$CH_3 \cdot CO(OCH_3) + NaHO =$$
$$\left. \begin{array}{l} CH_3 \cdot CO \\ CH_3 \cdot CO \end{array} \right\} O + H_2O =$$
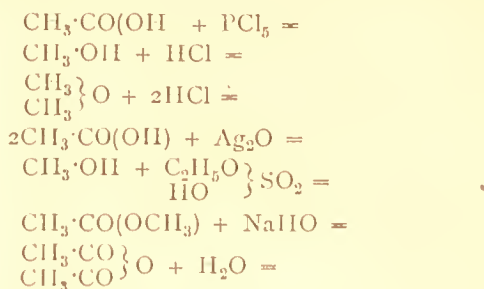
32. In what respect does prussic acid resemble and how does it differ from hydrochloric and hydrobromic acids?

33. ·3339 gram of a compound gave ·7896 gram of CO_2 and ·2924 gram H_2O. The vapour density (air $= 1$) was found to be 6·59. Calculate a rational formula.

34. ·1483 gram of ethylated acetone gave ·3799 gram of CO_2 and 1575 gram of water. Its vapour density (air $= 1$) was 2·951. Calculate the formula of the compound.

35. The analysis of barium diacetotartrate gave the following results :—

    I. ·2065 gram of substance gave ·1297 gram of $BaSO_4$.

    II. ·1377 gram of substance gave ·1307 of CO_2 and ·0300 of H^2O.

Calculate the formula of the salt and of the corresponding acid.

36. The following results were obtained in the analysis of the copper salt of ethyl-benzoic acid :—·2218 gram gave ·4827 gram of CO^2, ·1004 gram of water, and ·0489 gram of CuO. Calculate the formula of the acid.

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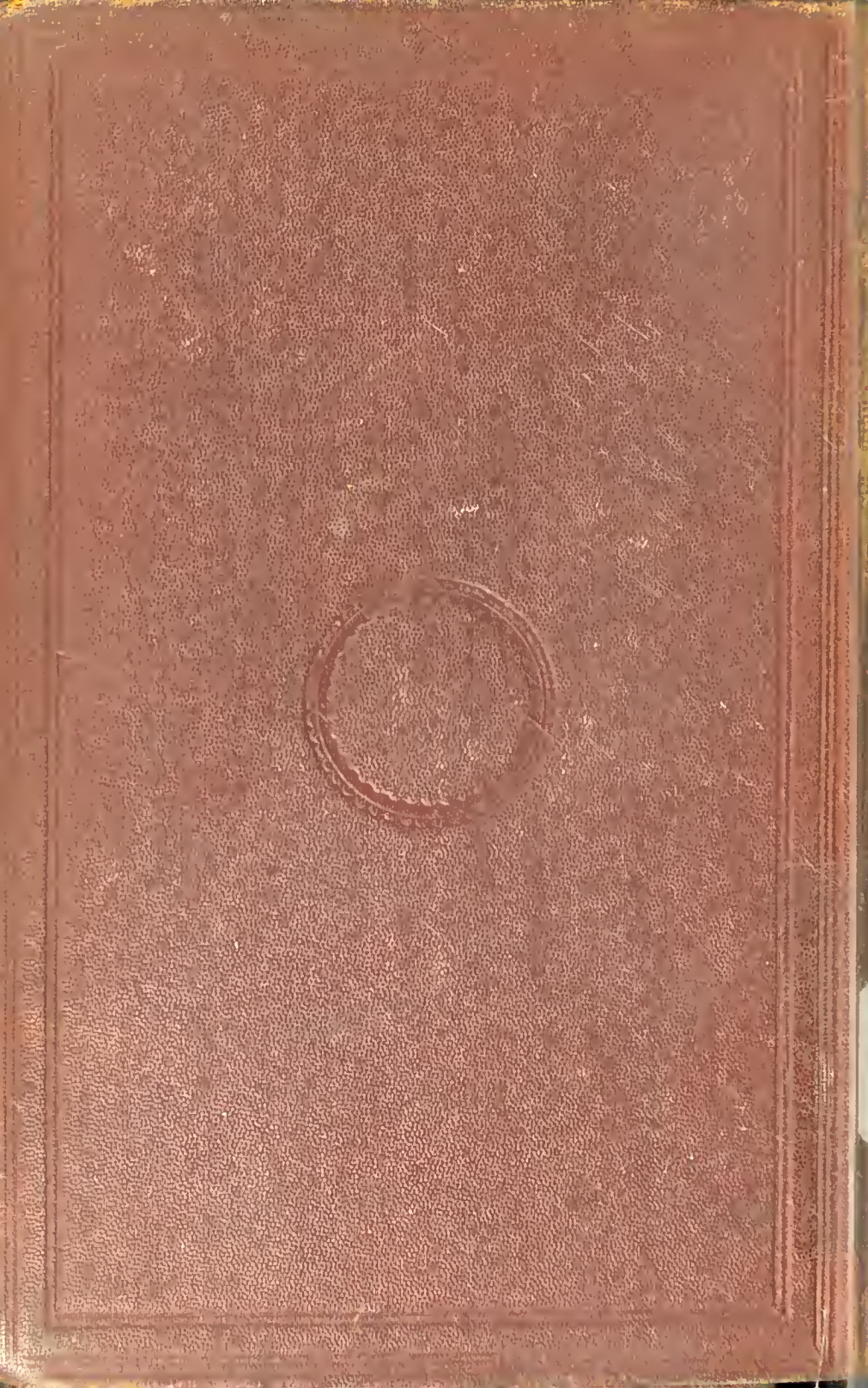
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